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Gaseous Heat Capacities

I. The Method and the Heat Capacities of C_2H_6 and C_2D_6

G. B. KISTIAKOWSKY AND W. W. RICE
Harvard University, Cambridge, Massachusetts

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An apparatus is described for the adiabatic expansion method of Lummer and Pringsheim, new features of which are a device for accurate and rapid pressure measurements and an effective design of the expansion vessel. The Wollaston wires, serving as a resistance thermometer, are subjected to extensive heat treatment which stabilizes their electrical characteristics so well that resistance changes accompanying gas expansion can be translated into temperature changes by means of separately determined temperature coefficients of resistance. The method here described is thus an absolute one and is not dependent on comparison with other gases of known heat capacity. Causes of imperfect temperature constancy after expansion are quantitatively discussed and traced to two processes: the heat conduction by the gas and the absorption of thermal radiation from the walls by the gas. Experimental data on air and carbon dioxide are presented and are compared with the theoretical values. Heat capacities of C_2H_6 and C_2D_6 are reported for the interval 0 to 90°C.

EXACT measurements of gaseous heat capacities, combined with those of reaction heats, provide the much needed empirical data for thermodynamic calculations of chemical equilibria; additionally, they serve as a valuable aid in the analysis of internal molecular motions from the Raman and infra-red spectroscopic data.

Unfortunately the experimental information on polyatomic gases is as yet quite scarce. Aside from a few scattered measurements, most of the experimental data has been obtained from the studies of the γ's of gases by the once rather popular velocity-of-sound method. It is now recognized, however, that the dispersion of sound in gases may invalidate some, if not all, of these values.

An extension of Eucken's "hot wire" method will be described in a paper following this. His procedure has been developed to a point where relative heat capacities over wide temperature ranges may be calculated from quite plausible assumptions concerning accommodation coefficients. But the hot wire method cannot be made entirely free of *ad hoc* assumptions and therefore an absolute method was required to check the other results and to obtain greater precision over at least a narrow temperature range.

For heat capacity measurements on limited samples of experimental materials the well-known Lummer-Pringsheim isentropic expansion method offers probably the best promise of success. In recent years quite a number of experimental procedures have been described, but in most instances the method has been developed as a relative one: instead of determining the true temperature change in the

expanding gas, the reading on the measuring instrument (Pt-wire or a thermocouple) was compared with a reading obtained in expanding a gas of known heat capacity. This procedure avoids a number of experimental complications, but it is open to the grave objection that the expansion may not have been carried out isentropically and that the measuring instrument may not have followed the gas temperature closely. Since both factors may change from gas to gas, the relative values involve systematic errors of unknown magnitude.

The Experimental Method

In many respects the apparatus adopted here is patterned after those described by Partington[1] and later by Eucken,[2,3] therefore only the new features need to be considered in detail. The general procedure is as follows. The gas is contained in a metal vessel of several liters volume at a pressure slightly above atmospheric. Two loops of very fine platinum wire of unequal length are connected to the opposing arms of a d.c. bridge with a 1 : 1 arm ratio and are suspended in the center of the metal vessel. The gas is rapidly expanded into the free atmosphere while the setting of the bridge is automatically changed so as to give a minimum deflection of the galvanometer upon expansion of the gas. The small residual deflection of the short period string galvanometer is recorded photographically. At the instant of expansion the galvanometer is momentarily disconnected from the circuit to prevent its damage. Before the expansion the galvanometer sensitivity is recorded on the same strip of film by temporarily shunting a small resistance (0.05 ohm) in the balanced bridge circuit. All these operations, including the opening of the expansion valve and the starting and stopping of the photographic drum, follow each other in predetermined time intervals, being controlled by magnetic switches operated by a constant speed motor. The whole cycle requires less than 10 seconds for completion.

The bridge was assembled from various parts in the laboratory, but a careful calibration against a Leeds & Northrup Mueller-type bridge showed it to be reproducible to 0.001 ohm. This included the resistances of all automatic switches and connecting wires. The switches were of light weight and of all-copper construction and were immersed in transformer oil. The entire circuit was carefully shielded from electromagnetic disturbances.

The flask was mounted in a large liquid thermostat, controlled to 0.01°, but constant to much better than this over the short time intervals involved in each measurement. The temperature was read with a multiple junction thermocouple calibrated *in situ* against a National Bureau of Standards certified platinum resistance thermometer.

Into the metal tube leading from the expansion vessel to the magnetically operated valve was inserted, by means of metal-to-glass seals, a section with three stopcocks, lubricated with Apiezon grease. One, of 12-mm bore, separated the valve from the expansion vessel. It remained open during heat capacity measurements but was needed to provide better vacuum in evacuation. The other, of similar bore, connected the vessel to the mercury diffusion pump and a third, of smaller bore, led to the gas filling, storage and purification (all-glass) systems and to the differential manometer. The valve connected with the free atmosphere through two large, liquid-air-cooled traps, which were filled with hydrogen during measurements. The expanded gas collected in the traps and after closing of this part of the system from the atmosphere, was vacuum distilled, purified and combined with the main sample.

One of the difficulties met with in practical executions of the Lummer-Pringsheim method is the necessity for accurate measurements of the pressure change on expansion. A differential manometer was built for this purpose and is sketched in Fig. 1. The manometer itself is a Bodenstein quartz spiral sealed into a glass tube provided with a plane window. To the end of the spiral, instead of the usual pointer, is sealed a platinized quartz microscope cover glass acting as a mirror. A beam of light from a straight filament lamp is reflected from the mirror and

[1] J. R. Partington, Proc. Roy. Soc. **A100**, 27 (1922).
[2] A. Eucken and Lude, Zeits. f. physik. Chemie **5B**, 413 (1929).
[3] A. Eucken and A. Parts, Zeits. f. physik. Chemie **20B**, 189 (1932–33).

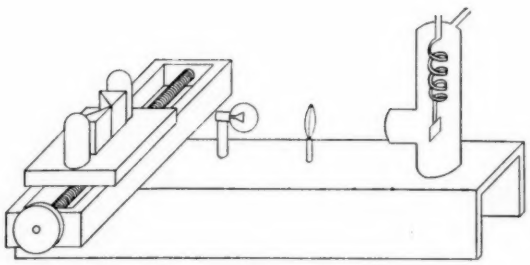

FIG. 1.

gives a narrow image parallel to the dividing line between two totally-reflecting prisms, behind which are two photo-cells. These are connected differentially to an amplifier employing a single D-96475 Western Electric tube and the Penick[4] circuit. The prisms with the photo-cells are mounted on the slide of a long micrometer screw, provided with a revolution counter and a divided head.

In use the outer glass tube of the spiral is open to the atmosphere, but the spiral itself is connected to the expansion vessel. Before the release of the expansion cycle the amplifier is balanced with grounded grid and then the screw is turned until balance is obtained again. At this setting the light is almost equally divided between the two photo-cells. Now the cycle is started, only a few seconds separating the pressure measurement and the expansion. Thus the objectionable temperature fluctuations of the thermostat and the atmospheric pressure changes are made innocuous. After the expansion the manometer is open to the atmosphere on both sides and the screw is turned until balance is obtained again, thus providing a zero point for the pressure measurement.

With about 30 cm optical path, one turn of the one-mm pitch screw was equivalent to about 0.42 mm pressure difference. The uncontrollable drifts of the zero point were quite regular, amounting to about 0.01 of a turn per hour, while the sensitivity of the instrument was such that 0.001 of a turn gave an observable deflection of the ordinary box-type galvanometer with a series resistance of five meg-ohms. All the essential parts of the instrument were attached to a piece of iron rail. This was mounted on a stone slab which rested, through felt, on an ordinary laboratory table. The entire instrument, together with the amplifier, was enclosed in an electrically shielded and a thermally lagged box. By improving the mounting, an even greater sensitivity and reproducibility of pressure readings could undoubtedly be obtained, but was not needed, since measurements of pressure to 0.001 mm were quite reliable and rapid. The instrument was calibrated against a wide tube decahydro-naphthalene manometer, contained in a thermally lagged box and read with a good cathetometer. The density of the liquid was determined. The systematic errors of this calibration were of the order of 0.05 percent and the reproducibility was better than 0.05 percent on a 20-mm pressure difference.

The second difficulty of the Lummer-Pringsheim method is a provision for an isentropic gas expansion correctly measured by a Pt-resistance thermometer. A rather extensive study of many forms of expansion vessels led to the selection of a cylinder, near the bottom of which were mounted two perforated plates with staggered one-mm holes distributed uniformly over the entire area about two to three cm apart. Below the baffle plates was the centrally located exit tube, two cm wide and about one meter long. The lead-in wires were sealed, by means of G-705-AJ glass and Kovar metal into a demountable section of the flat top of the expansion vessel. This section was then soldered to the vessel. To the three copper lead-in wires were welded three-cm lengths of thin Pt wire, the common battery connection being fashioned into an inverted T. To the four ends of these wires were soldered the Wollaston wires, the silver being dissolved from the Wollaston wires, after they were mounted, to within eight mm of the point of attachment. The loops were of V shape, small Pt weights holding them taut. One loop was *ca.* 12 cm long and the other, which served to cancel resistance changes near the supporting wires and near the stabilizing weight, was about five cm long.

To have the method function as an absolute one, the temperature coefficient of resistance of the wire must be known and must remain constant. The latter has been achieved by heating the wires electrically to a temperature at which their resistance is about three times the resistance

[4] D. B. Penick, Rev. Sci. Inst. **6**, 115 (1935).

at room temperature. After some 100 to 200 hours of annealing the wires are so well stabilized that long series of measurements can be carried out with the coefficient not changing by more than 0.1 percent. To determine it, the temperature of the thermostat was changed in 20 to 30° steps and the resistance of the wire was measured using the same bridge current as in subsequent heat capacity measurements. The point-to-point temperature coefficients were plotted and a smooth curve drawn. Individual points have been usually found to deviate by about 0.05 percent from the curve, but similar to the ordinary platinum thermometers, the Wollaston wires gave temperature coefficients decreasing with increasing temperature; a quadratic formula represents the resistance fairly well but not sufficiently accurately over the 100° temperature interval.

The extended heat treatment of the wires has another most beneficient effect: the surface of the rough Wollaston wires undergoes rather extensive sintering, as evidenced by a many-fold decrease of heat losses by radiation when the

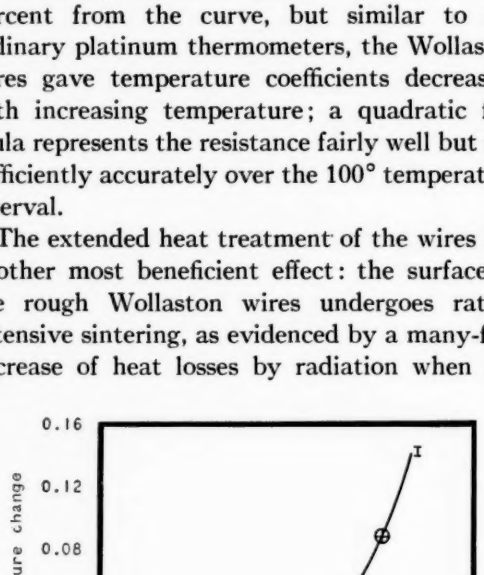

FIG. 2. Change of temperature of gas after expansion. (I) is the theoretical curve for air calculated from Eq. (1), and ⊕ the observed experimental points. (II) are the experimental points for ethane.

wire is heated in vacuum above the temperature of the surroundings. After the gas expansion the temperature of even an infinitely thin wire is somewhat higher than that of the surrounding gas, because it receives heat by radiation from the warmer walls of the enclosing vessel. In the first approximation this radiation correction is equal to the temperature difference between the gas and the walls, times the ratio of heat conductances from the wire in vacuum and in the gas at atmospheric pressure. With annealed wires these ratios are exceedingly small; thus with ethane at 0°C a ratio of 0.00098 was found. With the better annealed wire, with which the main series of measurements were made, ethane at 90° gave 0.0014 and air 0.00196. These figures make the radiation correction so small that the theoretical difficulties met with in deducing its true magnitude, as discussed for instance by Eucken and Lude,[2] are reduced to insignificance.

Because of finite thickness of the wires, an error may arise through incomplete temperature equalization between the wire and the gas after expansion. To test this, experiments were made with wires of 0.005, 0.0075 and 0.010 mm diameter. The two thinner wires showed indistinguishable behavior with a galvanometer of 0.2-sec. period, while the heaviest one gave indications of noticably slower heat exchange. The regular measurements were made therefore with the 0.0075-mm wire which gave higher electrical sensitivity for the same temperature difference between the wire and the gas. The heating of the wire by the bridge current may itself introduce errors because after the expansion the gas is not perfectly still and its apparent heat conductivity may be greater. Normally all experiments were made with the wire 0.01° warmer than the gas but a few experiments in which the wire was about 0.04° warmer gave results differing from the mean by not more than the usual scattering of data; this effect, therefore, does not contribute to errors.

Partington[1] contends that in order to obtain constancy of temperature after expansion, very large expansion vessels must be used, he himself employing one of 130 liters capacity. Eucken[2] uses a small vessel but his temperature characteristics are far from perfect. We have found that with a vessel of 12 liters of the earlier described design, excellent flats of several seconds duration could be obtained with air. Contrary to Partington's experience, in our setup the speed of expansion seems to have no effect on the appearance of the flats (nor, we may add perhaps, on the values of heat capacities). The position, shape and method of mounting of the Wollaston wires, however, are somewhat critical as regards the appearance of the records, although not that of the resultant heat

capacities if the temperature of the wire extrapolated to the instant of expansion is taken for their calculation. Exact instructions for the best design of the Wollaston loops are difficult to give, but the most nearly symmetrical arrangement as far away as possible from all solid parts of the apparatus seem to give the best results.

Unfortunately the 12-liter vessel was too large to be used with the limited supply of C_2D_6 on hand and another one, of three-liter capacity, had to be constructed. Here the uncompensated part of the wires was only *ca.* 4.5 cm away from the nearest obstruction and the flats were decidedly poorer. Unexpectedly air gave the best records. Under ideal conditions the temperature of the wire is changed after expansion only by the inevitable conduction through (still) gas. This can be calculated under some simplifying conditions,[5] the temperature at the center of an infinite cylinder of radius R at a time t, provided at a time zero the gas in the cylinder is at a uniform temperature T_0 and the walls of the cylinder are at a temperature $T_0+\Delta T$ being given by the following equation:

$$T_{(R=0)}=T_0 +\Delta T_0\left[1-2\sum_N \frac{\exp\left(-k/R^2(\alpha_n R)^2 t\right)}{J_1(\alpha_n R)(\alpha_n R)}\right]. \quad (1)$$

Here k denotes the ratio of thermal conductivity and of the heat capacity of the gas times its density. $T_{(R=0)}$ is the temperature at the center at time t. The wall temperature is assumed to remain constant. $(\alpha_n R)$ is the nth root of the equation $J_0(\alpha_n R)=0$. $J_1(\alpha_n R)$ is the Bessel function of the 1st order. Fig. 2 shows a typical change of wire temperature after expansion, together with the theoretical curve calculated from Eq. (1). Up to about four seconds the agreement of the two is excellent, showing that with air the expansion vessel functions almost as an ideal system until convection sets in.

With gases other than air (carbon dioxide and ethane; also several C_3 hydrocarbons dealt with in the next publication of this series) the wire temperature was found to change more rapidly than demanded by Eq. (1). In particular, the temperature did not remain constant even in the first seconds after expansion. After deduction of a term demanded by Eq. (1) a roughly linear change of temperature with time remained (see Fig. 2, curve 2). Many modifications of the vessel design and of the conditions of expansion did nothing to remove this difficulty and finally all calculations were made by extrapolating the wire temperature to the instant of expansion (see Fig. 3). The rate of the linear temperature change increases so rapidly with the temperature of the system that at the lower end of the temperature range covered in this work the extrapolation is quite unimportant. At 90°C, however, it reaches almost 0.5 percent of the total temperature change and adds perhaps as much as 0.2 percent to the uncertainty of the results.

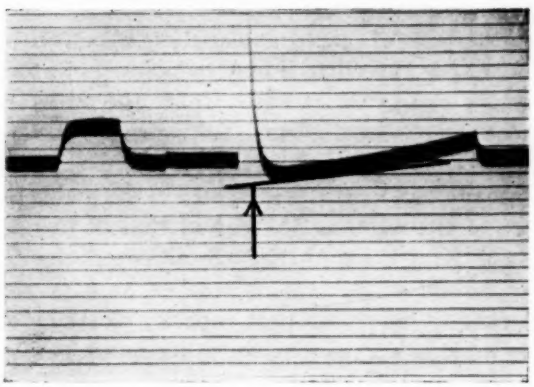

FIG. 3. Resistance change of the wire after gas expansion (C_2H_6 at 363°K) and the extrapolation to zero time.

In the meantime we believe we have found an adequate explanation of this effect and hope to eliminate the difficulty in future work. It will be noted that all gases showing the described behavior have absorption bands in the infra-red. Since the absorption coefficients are in general moderate, the radiation from the warmer walls of the enclosing vessel must be absorbed throughout the gas volume and thus will cause an approximately linear temperature change instead of an exponential dependence on time as demanded by Eq. (1) and, in fact, by any other material mechanism of heat conduction from the walls. Experiments with gold-plated mirror-like inner surface of the expansion vessel, which we hope to make in the near future, may show

[5] Carslaw, *Conduction of Heat* (Macmillan, 1922), p. 222.

TABLE I. *Heat capacity of C_2H_6 at 336.6°K. Temperature coefficient of resistance 1.1004 ohms/degree. Radiation correction is 0.116 percent of the observed temperature change.*

T_i	P_{FINAL} MM	ΔP_{MM}	ΔT_{EXTRAP}	$\Delta T_{\text{CORRECTED}}$	C_p' CAL. °K MOLE^{-1}
336.605	780.45	15.804	0.002	0.982	13.617
336.605	780.60	22.482	0.007	1.392	13.609
336.604	780.45	31.461	0.006	1.935	13.616
336.604	780.35	35.689	0.008	2.187	13.627
336.604	780.25	22.122	0.003	1.373	13.593
					Av. 13.613 ±.009

whether the advanced explanation is correct or not. In the meantime it may be pointed out that enough energy is radiated from the walls to cause the observed effects. Taking as the surface of the flask 1120 cm², the Stephan constant as 5.7×10^{-5} erg cm^{-2}, deg.$^{-4}$, sec.$^{-1}$, the temperature of the walls as 363°K and that of the gas as 362°K, it is found that 0.3 cal. enters the gas per second if the wall is treated as a perfect blackbody. Since the heat capacity of ethane in the flask is 1.5 cal./degree, a maximum rate of heating of 0.2°/sec. may be obtained. Actually observed were rates of about 0.01 to 0.02°/sec. when the temperature difference between the gas and the walls was 1 to 2°. In view of the imperfect blackness of the walls (darkened unpolished brass) and of the incomplete absorption of radiation by the gas the two figures stand in a reasonable ratio to each other.

Thermodynamics demands that the relation between pressure and temperature in an isentropic expansion be of the form:

$$C_p\left(\frac{dT}{dP}\right)_s = T\left(\frac{dv}{dT}\right)_p \tag{2}$$

or written for ideal gases

$$C_p'\frac{dT}{T} = R\frac{dp}{p}. \tag{2a}$$

Ordinary gases show sufficiently large deviations from ideality to make Eq. (2a) unsuitable for accurate calculations. The obvious next approximation is to use the simplified Virial Equation of State:

$$PV = RT + BP.$$

If the heat capacity at infinitely low pressure is denoted by $C_p°$, that at the mean pressure of the experiment by C_p and the changes of temperature and pressure treated as so small that C_p, dB/dT, and d^2B/dT^2 are constant over the ranges of integrations, the following equations result:

$$C_p^0 = \frac{R\ln P_i/P_f}{\ln T_i/T_f} - \frac{\Delta P dB/dT}{\ln T_i/T_f} + T_{av}P_{av}\frac{d^2B}{dT^2}, \tag{3}$$

$$C_p = \frac{R\ln P_i/P_f}{\ln T_i/T_f} - \frac{\Delta P dB/dT}{\ln T_i/T_f}, \tag{3a}$$

$$C_p' = \frac{R\ln P_i/P_f}{\ln T_i/T_f}. \tag{3b}$$

These have been used in all subsequent calculations, the values of the temperature derivatives of the virial coefficients being obtained from several equations of state, as explained later in detail.

Air used in preliminary experiments was dried and freed from carbon dioxide by passage through long tubes filled with Dehydrite and with Ascarite.

TABLE II. (*A*) *Heat capacity of dry air and* (*B*) *heat capacity of carbon dioxide.*

NO. OF RUNS	T_{AV}	RANGE OF Δp MM	P_{FINAL} AVERAGE MM	RAD. CORR.*	$\frac{dR}{dt}$ OHM DEGREE	C_p'	C_p	C_p^0 CAL. MOLE	C_p^0 THEORETICAL
(A)									
4	271.36	42.316–20.702	765.48	*0.14%	1.2246	6.911	6.928	6.913±.009	6.941
4	298.30	40.658–17.418	755.56	*0.22%	1.2170	6.943	6.956	6.945±.008	6.956
5	342.69	33.283–16.328	761.60	*0.40%	1.2005	6.965	6.974	6.966±.008	6.965
6	366.42	42.048–18.170	755.10	*0.47%	1.1933	6.983	6.990	6.984±.02	6.980
(B)									
4	300.06	37.619–22.531	751.10	0.13%	1.1110	8.868	8.976	8.903±.013	8.910
4	331.86	37.965–25.293	780.20	0.16%	1.1013	9.210	9.296	9.240±.010	9.242
5	367.72	36.571–22.780	765.75	0.174%	1.0882	9.571	9.635	9.595±.007	9.599

* These measurements were made with a wire not so thoroughly annealed as those reported in Tables IV and V; whence the larger radiation corrections.

Carbon dioxide was taken from a tank marked as 99.5 percent pure. It was condensed in liquid air, the first fraction pumped away and the middle portion used for measurements.

Ethane was prepared by hydrogenation of a 99.5 percent pure ethylene[6] over a copper catalyst under conditions eliminating side reactions.[7] The ethane was condensed in liquid air and subjected to repeated vacuum distillations from bulb to bulb, only the middle fraction being retained for measurements.

The preparation and estimates of purity of the deuterated ethane are discussed in the following article of Dr. F. Stitt, to whom we are indebted for this material.

The Results

Table I gives the details of one series of measurements on ethane and illustrates the procedure and the magnitude of the various corrections applied to the immediate results of an experiment. In Table I, T_i indicates the temperature of the gas before expansion, P_f and ΔP the final pressure and the pressure change; ΔT_{extrap} is the correction applied in extrapolating the wire temperature to the instant of expansion from the galvanometer readings; ΔT_{corr} is obtained on division of the observed resistance change by the temperature coefficient of resistance and application of the two corrections given in Table I. It will be noted that these corrections are sufficiently small to make the method a truly absolute one. Furthermore it is to be noted that no correlation between the pressure change in expansion and the values of the heat capacity exists. We believe this to be an additional assurance of the essential correctness of the described procedure.

The average deviations from the mean in this and in other series are of the order of 0.1 percent and at most twice this amount should be allowed for systematic errors, so that the results are accurate to better than 0.3 percent.

Table II gives condensed results on air and carbon dioxide, together with the statistically calculated heat capacities. The second virial coefficients of air and of carbon dioxide were calculated from Berthelot's equation of state as given by Partington.[1] Statistical values of the heat capacities were obtained by the usual formulas for harmonic oscillators from vibrational data given in Sponer's *Molekülspektra*. The results for carbon dioxide were compared with the values obtained by Kassel[8] for 300 and 400°K, who used the exact summation of the true quantum levels. Linear interpolation of the small differences (0.02 to 0.04 cal./mole) was used to convert our simplified calculations at all intermediate temperatures. The errors arising from this procedure should be entirely insignificant.

Table III. *(A) Air and (B) carbon dioxide.*

T°K	C_p^0 Statistical	C_p^0 K and R	C_p^0 E and L	C_p^0 Partington
(A)				
271.2	6.941	6.913	6.909	
290.1	6.951	6.937		6.914
292.7	6.953	6.939	6.964	
384.0	6.993	6.998	6.967	
(B)				
292.9	8.835	8.827	8.774	
358.4	9.505	9.503	9.528	

For both gases the experimental data agree to within 0.2 percent with the theoretical values. This justifies the claim, made above, that for other gases also the heat capacities reported here are accurate to better than 0.3 percent.[9]

Eucken and Lude[2] also have measured the heat capacities of air and carbon dioxide in the temperature range covered in Table II. Table III gives their data together with values interpolated from Table II, statistical calculations and a value of Partington.[1] The agreement between theory and experiment is considerably better for the here reported measurements, although the

[6] Chief impurity stated to be air; diethyl ether also present.

[7] Kistiakowsky, Romeyn, Ruhoft, Smith and Vaughan, J. Am. Chem. Soc. **37**[1], 71 (1935).

[8] L. S. Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).

[9] A series of runs on CO_2, made at the beginning of this work, gave results lower by about 0.4 percent than those reported in Table II. Fewer precautions were taken then to purify carbon dioxide but, most important of all, the technique of annealing the wires was not properly developed and the temperature coefficients of the electrical resistance drifted considerably. Better annealed wires were used in all experiments on ethane, and a few check runs made at the end of the work agreed perfectly with the earlier experiments. Because of all this we feel fully justified in disregarding the first series of runs on carbon dioxide, although unable to give the precise reasons for its systematic deviations.

TABLE IV. *Heat capacity of ethane* (C_2H_6).

No. of Runs	T_{AV}	Range of Δp mm	P_{FINAL} Average mm	$\frac{dR}{dt}$ Ohm / Degree	Rad. Corr. Percent	C_p'	C_p	C_p^0 Cal. °K Mole^{-1}
6	272.07	41.796–27.666	761.38	1.2246	0.098*	11.691	11.958	11.834±.010
5	302.70	44.224–24.762	758.55	1.2156	0.20*	12.613	12.824	12.733±.016
5	335.82	35.689–15.804	780.40	1.1003	0.116	13.612	13.788	13.719±.009
5	364.78	32.352–18.685	770.00	1.0893	0.14	14.497	14.644	14.589±.025

* The wire used in these measurements was annealed less extensively.

TABLE V. *Heat capacity of ethane* (C_2D_6).

No. of Runs	T_{AV}	Range of Δp mm	P_{FINAL} Average mm	$\frac{dR}{dt}$ Ohm / Degree	Rad. Corr. Percent	C_p'	C_p	C_p^0	C_p^0 Corrected for 0.5 Percent Light H_2
6	272.23	43.857–31.557	765.50	1.2246	0.11*	14.133	14.300	14.276	14.289±.018
5	304.06	42.976–33.497	764.20	1.2126	0.21*	15.471	15.682	15.591	15.605±.017
4	334.90	22.175–27.406	766.60	1.1002	0.11	16.819	16.995	16.926	16.942±.018
7	365.97	33.294–21.184	751.11	1.0888	0.13	18.089	18.236	18.181	18.199±.020

* The wire used in these measurements was annealed less extensively.

temperature coefficients of the presently used wires were not calibrated by another gas as the German workers have done.

The Table IV gives data on ordinary ethane. Correction to ideal state was made with the aid of coefficients taken from Eucken and Parts.[3] The agreement of these data with those of Eucken and Parts is very good, the maximum difference being less than 0.3 percent.

Table V presents data on C_2D_6. The same equation of state was used for it as for ordinary ethane, but the resultant values of the heat capacity were further corrected for the 0.5 percent of light hydrogen present as C_2D_5H (cf. the following paper by F. Stitt). The correction factor was obtained by assuming that the heat capacity of ethane, between the extremes of C_2H_6 and C_2D_6, is a linear function of the deuterium content. The ensuing error is undoubtedly quite small in view of the smallness of the entire correction.

In the following paper the heat capacity data on ethanes will be discussed; therefore we shall refrain from further comments at this point.

The Low Temperature Gaseous Heat Capacities of C_2H_6 and C_2D_6

G. B. KISTIAKOWSKY, J. R. LACHER* AND FRED STITT†
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts
(Received February 4, 1939)

The heat capacities of gaseous C_2H_6 and C_2D_6 have been measured down to 93°K with the low pressure thermal conductivity apparatus previously described. An improved cryostat and better designed conductivity cells were used. A new method of obtaining the heat capacities from the thermal conductivity data is described which does not require a knowledge of the accommodation coefficient α. It is based on the assumption that when the accommodating efficiency of the wire is changed, α changes in the same direction for the gases being compared and further that the percentage change in α is greater the more its absolute value deviates from unity. It is then possible to show that the unknown α for the gas being studied can be bracketed within narrow limits by the α's of comparison gases. The heat capacity results for light and heavy ethane indicate a potential barrier restricting internal rotation of essentially sinusoidal shape and with a depth of 2750 cal./mole.

AN EARLIER communication from this laboratory[1] on the same subject reported measurements of the heat capacity of ethane at 163 and 143°K. These measurements are now extended to cover the range from 94 to 335°K; measurements over the same temperature range on deuterated ethane are also presented.

As before, the thermal conductivity method was used, in which the heat conducted from a "hot wire" is compared for two gases when they are at equal pressures and when the same temperature difference exists between the wire and the surrounding wall. If the mean free path of the gas molecules is very large compared to the diameter of the wire, the ratio of the heats conducted is related to the heat capacities by:[1]

$$\frac{Q'}{Q''}=\frac{\alpha'}{\alpha''}\frac{(C_v'+R/2)}{(C_v''+R/2)}\left(\frac{M''}{M'}\right)^{\frac{1}{2}}. \qquad (1)$$

Here Q is the heat conducted by a gas; α is the mean accommodation coefficient; C_v is the mean heat capacity and M is the molecular weight. Eucken[2] assumed that at low temperatures the accommodation coefficient ratio approaches unity and that therefore the heat capacity of one gas may be calculated if that of the other is known. At higher temperatures the ratio is in general different from unity and Eucken's procedure does not allow the calculation of the unknown heat capacity. This difficulty has now been overcome as will be shown on the following pages.

Experimental Details

The general procedure in the present experiments was similar to that employed before,[1] but several changes are worthy of note. The most important of these lay in the construction of the thermoconductivity cells. The platinum wire, of 0.025-mm diameter, was mounted coaxially in a Pyrex tube of three-mm internal diameter. To both ends of the wire were fused short lengths of 0.05-mm platinum wire. One end was then silver-soldered to a small spiral tungsten spring brazed to a tungsten seal; the other end was fused to a short piece of a 0.2 mm-platinum wire which, in turn, was silver-soldered to a tungsten seal. The intermediate platinum wires were found necessary to avoid breakage at the joints between the fine wires and tungsten.

Two such units comprised a cell. They were identical in every respect, except that one was longer, having a 20-cm piece of the 0.025-mm wire between the seals and the other was shorter with only four cm of the fine wire. The two were mounted side by side in the cryostat and were placed in the opposing arms of a Leeds & Northrup Mueller-type bridge which has arms of equal resistance and which was kept balanced at all times. The battery connection to the cells was

* Present Address: Department of Chemistry, Brown University.
† National Research Fellow in Chemistry.
[1] G. B. Kistiakowsky and F. Nazmi, J. Chem. Phys. **6**, 18 (1938).
[2] A. Eucken and A. Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

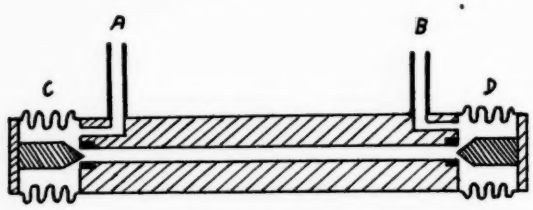

FIG. 1. Gas pipette. Tubes *A* and *B* lead to a controlled-pressure gas supply and to the conductivity cell systems, respectively. *C* and *D* are sylphon bellows. Light shading indicates brass, heavy shading steel, and solid black monel metal.

at their lower ends, in the cryostat liquid, the electrical circuit being grounded at this point. The upper connections to the cells were insulated by glass from the liquid bath. With this arrangement the resistance measured by the bridge is that of the central portion of the long wire only; all other resistances cancel out. A simple calculation taking into account the heat conductance along the wire and heat losses by gas conduction and thermal radiation shows that the temperature of the measured 16-cm portion of the long wire should be constant to within a few percent, except in vacuum at low temperatures. Since the measurements consist substantially in the comparison of the electrical energy inputs required to keep the wire at a constant resistance when one gas in the cell is replaced by another, the present construction of the cells, providing a nearly constant temperature along the measured portion of the wire, insures that the measurements are not complicated by variable temperature distribution. It is true that the temperature even along the central portion of the wire is not *exactly* constant, but its distribution changes so little when one gas is replaced by another, that the resultant effects should be considerably less important than some other sources of experimental error. Further advantage of the present construction of the cells is that owing to the small exposed area less gas is adsorbed on the walls when the cryostat is cold.

The conductivity cells were connected to a thermostated 12-liter flask and the gas pipettes. Three cells were used, one of which served as a Pirani gauge and was kept in an ice bath. The wires in the Pirani gauge and in cell no. 1 consisted of blank drawn platinum. Those in cell no. 2 were coated electrolytically with platinum black. The wires were annealed by electric heating in vacuum for ten hours at a temperature of about 500°C. The accommodation coefficient ratios on these wires agreed excellently with those measured previously[1] on similar unannealed wires. The new wires showed, however, no measurable resistance drift with time.

The gas pipette was essentially a double metal valve (Fig. 1). Absence of stopcock grease and the positive seating of the steel plungers maintained the free space of the pipette (some tenths of a cc) rigidly constant and it was not necessary as before to expand the gas in several stages. Instead the pipette was filled directly with the supply gas at about 300 mm and then connected to the conductivity cell system. All metal joints were leaded and metal-to-glass seals used so that the valves could be baked out in vacuum. By means of stopcocks the pipette was cut off from the cell system while not in use and put in communication with the pumps.

The cryostat, as before, consisted of two Dewar cylinders, but now the outer one held the cooling agent and the inner one was the thermostat proper, with the cells, heater and stirrer mounted in it. As described before[1] the pressure of the gas between the walls of the inner Dewar was regulated automatically to compensate for losses of the cooling agent. Temperature was controlled by a platinum resistance thermometer with the usual bridge-galvanometer-photoelectric cell-relay system. The reversal of the roles of the two Dewars was necessary at low temperatures, heat conduction from the outside being so large that it would have been difficult to maintain the outer Dewar at the desired temperatures.

The electric circuit for the conductivity cells was the same as previously described.

In addition to heat conductivities of ethane and deuterated ethane, also those of ethylene and

TABLE I. *Effect of pressure on heat conductance. Cryostat temperature 145.4°K; wire (No. 2) temperature 169.2°K. One pipette of gas raises the pressure 2.4×10^{-3} mm* Hg.

No. of Pipettes	Q'' C_2H_4	Q' C_2D_6	Q'/Q''
1	930	1082	1.163
2	1927	2250	1.168
3	2974	3474	1.168

carbon dioxide were measured for comparison purposes. The heat capacity of carbon dioxide was calculated as described in the preceding paper.[3] Those of ethylene and ethane above 192°K were taken from the preceding paper[3] and from that of Eucken and Parts.[2] Below 192°K the heat capacity of ethylene was calculated statistically using vibrational frequencies given by Linnett.[4]

Carbon dioxide was prepared as described in the preceding paper.[3] Ethane was prepared by hydrogenation of 99.5 percent C_2H_4 over a platinum catalyst, and purified by fractionation. Ethylene was a part of the very pure sample used for heats of hydrogenation measurements in this Laboratory.[5] The preparation of the deuterated ethane is described in the following paper.

The method of calculating heat conductances from experimental data was identical with that described previously.[1]

Experimental Results

Table I illustrates the observed dependence of the Q's (in arbitrary units) and of their ratios on pressure. It is evident that the heat conducted by two or three pipettes of gas is greater than two or three times the heat conducted by a single pipette of gas at the low temperature represented in Table I. Measurements on the Pirani gauge showed, however, that the pressures of the gases increased proportionately to the number of pipettes admitted. Hence the observed effect must be due to thermal transpiration,[6] which increases with decreasing temperature of the conductivity cells. Indeed, when the cryostat was above the temperature of the 12-liter flask, the heat conducted per pipette was found to decrease when more gas was added. Owing to the similar kinetic properties of C_2H_4 and C_2D_6, however, the ratio Q'/Q'' was experimentally found to be independent of pressure, making unnecessary an extrapolation to the infinitely dilute state.

When the cryostat was above 134°K, the ratio of the heat conductances of ethane and ethylene read on the Pirani gauge was independent of the cryostat temperature and of the gas pressure showing that no differential adsorption took place. At lower temperatures of the cryostat the Pirani gauge gave evidence of adsorption. In order to correct for this, the following relation was used:

$$(Q'/Q'')_{\text{corr}} = (Q'/Q'')_{\text{exp}} \frac{(Q'/Q'')_{P.R.}}{(Q'/Q'')_{P.E.}}. \qquad (2)$$

Here $(Q'/Q'')_{\text{exp}}$ is the direct result of measurements with the cryostat at some low temperature; $(Q'/Q'')_{P.R.}$ is the ratio measured on the Pirani gauge when the cryostat is at room temperature and no differential adsorption takes place, while $(Q'/Q'')_{P.E.}$ is the experimental ratio found with the Pirani gauge when the cryostat is at a temperature at which adsorption occurs. The ratio of the last two quantities will be called the Pirani factor and is listed as such in the tables.

Equation (2) is based on the assumption that even at low temperatures the heat conducted is a linear function of the pressure of the gas in the 12-liter flask. While the data in Table I show this to be not strictly true, the equation is sufficiently accurate for *small* differences of adsorption. This was confirmed experimentally by finding that Q'/Q'' calculated in this way was independent of a threefold variation in pressure.

Although ethane is in general more abundantly adsorbed than ethylene, the first pipette of gas added after the cells had been evacuated and then cooled to low temperatures, was adsorbed more strongly than subsequent pipettes independent of whether the gas was ethylene or ethane. Pumping out this gas and repeating gas admission resulted in lesser adsorption. Evidently at these temperatures there forms on the surfaces of the conductivity cells a layer of adsorbed gas which is less adsorbing than the surface offered to the gas when the cells are evacuated at room temperature.

After cooling the evacuated cells in run no. 5 to 93°K, ethane was admitted before ethylene

[3] G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **7**, 281 (1939).

[4] Unpublished work. The heat capacity calculated using Linnett's set of vibrational frequencies differs by less than 0.03 cal. from that found using the frequencies given by Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

[5] G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, J. Am. Chem. Soc. **57**, 65 (1935).

[6] See, for example, M. Knudsen, Ann. d. Physik **31**, 633 (1910); J. K. Roberts, Proc. Roy. Soc. London **A135**, 194 (1932).

TABLE II. *Heat capacities of* C_2H_6 *at low temperatures.**

MEAN OF WIRE AND BATH TEMPERATURES, °K	NO. OF PIPETTES ADMITTED	$(Q'/Q'')_{corr}$	PIRANI FACTOR	C_v'' CAL./MOLE	C_v' CAL./MOLE
WIRE NO. 1					
100.5	1	1.058	0.993	(5.97)	6.63
100.5	2	1.062	1.016	(5.97)	6.66
100.5	1	1.122	1.099	(5.97)	7.09†
100.5	2	1.058	1.038	(5.97)	6.63
98.4	1	1.051	1.044	(5.97)	6.58
98.4	2	1.052	1.050	(5.97)	6.59
98.4	3	1.056	1.084	(5.97)	6.62
94.3	1	1.044	0.993	(5.97)	6.53
94.3	2	1.050	1.016	(5.97)	6.57
94.3	1	1.111	1.099	(5.97)	7.01†
94.3	2	1.046	1.038	(5.97)	6.55
93.1	1	1.043	1.063	(5.97)	6.52
93.1	2	1.038	1.053	(5.97)	6.49
93.1	3	1.043	1.084	(5.97)	6.52
WIRE NO. 2					
134.1	1	1.126	1.005	(6.04)	7.21
134.1	2	1.128	1.006	(6.04)	7.22
134.1	3	1.129	1.009	(6.04)	7.23
99.6	1	1.057	0 993	(5.97)	6.62
99.6	2	1.060	1.016	(5.97)	6.65
99.6	1	1.124	1.099	(5.97)	7.11†
99.6	2	1.059	1.038	(5.97)	6.64
97.4	1	1.053	1.044	(5.97)	6.60
97.4	2	1.053	1.050	(5.97)	6.60
97.4	3	1.051	1.084	(5.97)	6.58
93.5	1	1.044	0.993	(5.97)	6.53
93.5	2	1.046	1.016	(5.97)	6.55
93.5	1	1.113	1.099	(5.97)	7.03†
93.5	2	1.049	1.038	(5.97)	6.58
92.4	1	1.053	1.063	(5.97)	6.50
92.4	2	1.056	1.053	(5.97)	6.62
92.4	3	1.040	1.084	(5.97)	6.50

SUMMARY

T°K	134.1	100.5	99.6	98.4	97.4	94.3	93.5	93.1	92.4
$(C_v)C_2H_6$ Wire No. 1		6.64		6.60		6.55		6.51	
$(C_v)C_2H_6$ Wire No. 2	7.22		6.64		6.59		6.55		6.57

* Accommodation coefficient ratios assumed unity; primes refer to ethane, double primes to ethylene; bracketed values assumed. At 134°K one pipette of gas raised the pressure 4.9×10^{-3} mm Hg; at all other temperatures another pipette was used, admitting 2.4×10^{-3} mm.

† All these values were determined with the same gas filling; evidently a gross error was made in measuring the Pirani factor, since the addition of another pipette (next line) gave normal values. These heat capacities were not used in averaging.

and the Pirani factor for one pipette was 1.063. However, in run no. 17 at 94°K (performed some two months later) ethylene was admitted first and was the more adsorbed, as shown by the Pirani factor of 0.993. Nevertheless the heat capacities of ethane calculated from the two experiments agree excellently: 6.52 cal./mole at 93.1°K and 6.53 cal./mole at 94.3°; this constitutes an added proof of the validity of Eq. (2). Of course with large differences of adsorbabilities and of molecular diameters of the compared gases Eq. (2) should cease to be valid.

It should be noted that although adsorption occurred, the pressure in the cells was definite and showed no tendency to drift, provided not more than three pipettes of gas were added.

Temperature difference between the wire and the walls of the cells was also found not to affect the results. For example in run no. 5 with wire no. 1 and a temperature difference of 7.21° the heat conducted by three pipettes of ethane per degree temperature difference was 212.1; with a temperature difference of 17.69° it was 191.7. For ethylene, the same temperature differences and quantities of gas added gave conductances of 220.5 and 197.7, respectively. The ratios, Q'/Q'' of Eq. (1), are 0.962 and 0.970. The small difference of these values is largely due to the greater mean heat capacity of ethane when the wire temperature is higher: 6.52 and 6.62 cal./mole at 93.1 and 98.4°K, respectively, are obtained if the accommodation coefficient ratios are taken as unity. It is to be noted, however, that while the ratio of heats conducted by two gases satisfies Eq. (1), the thermal conductance of each gas is not strictly proportional to the temperature difference between the wire and the walls.

At the higher temperatures where the heat capacities of ethane and ethylene are both known, the accommodation coefficient ratios calculated from the present measurements agreed completely with those reported previously[1] and therefore need not be presented in detail. As before it was found that the platinized platinum wire gives ratios much closer to unity than does the bare wire. On both wires the ratios approach unity with decreasing temperature. It was safe therefore to assume that at 134°K and lower temperatures the ratios are equal to unity, the error resulting from this assumption being certainly less than one percent. Table II shows the heat capacities of ethane calculated on this assumption. It is to be noted that both wires give consistent results.

Heat transfer in C_2D_6 was compared with that in C_2H_6, C_2H_4 and CO_2. Since at the time of these measurements the heat capacity of C_2D_6 was not known at any temperature, the experimental results were used in Eq. (1) to calculate the quantity:

$$Y_x=(C_v+R/2)_{C_2D_6}\frac{\alpha_{C_2D_6}}{\alpha_x}$$

$$=\frac{Q_{C_2D_6}}{Q_x}(C_v+R/2)_x\left(\frac{M_{C_2D_6}}{M_x}\right)^{\frac{1}{2}}, \quad (3)$$

where x refers to the comparison gas. Table III presents the results for the temperature range from 214 to 336°K. It is evident from the table that $Y_{C_2H_6}$ and $Y_{C_2H_4}$ are smaller on the bare wire no. 1 than on wire no. 2, while Y_{CO_2} is larger on the bare wire. To interpret this observation it will be assumed that all accommodation coefficient ratios approach unity on changing from the bare to the platinized wire. This assumption is supported by experimental work in this laboratory on C_2H_4, CO_2, C_2H_6, allene and cyclopropane (the latter two unpublished) and is also confirmed by the data of the preceding paper[3] in the range from 273 to 336°K. The data of Table III show then that $\alpha_{C_2D_6}$ is less than either $\alpha_{C_2H_4}$ or $\alpha_{C_2H_6}$, but is greater than α_{CO_2}. Hence:

$$\left[\frac{\alpha_{C_2D_6}}{\alpha_{C_2H_4}}\right]_{\text{wire no. 1}} < \left[\frac{\alpha_{C_2D_6}}{\alpha_{C_2H_4}}\right]_{\text{wire no. 2}} < 1$$

$$< \left[\frac{\alpha_{C_2D_6}}{\alpha_{CO_2}}\right]_{\text{wire no. 2}} < \left[\frac{\alpha_{C_2D_6}}{\alpha_{CO_2}}\right]_{\text{wire no. 1}}$$

and since, as this and previous research[1] has shown,

$$\frac{\alpha_{C_2H_6}}{\alpha_{C_2H_4}} > 1$$

it follows that:

$$\alpha_{C_2H_6} > \alpha_{C_2H_4} > \alpha_{C_2D_6} > \alpha_{CO_2} \qquad (4)$$

on both the bare and the platinized wires. Eq. (4) limits the values of the accommodation coefficients of deuterated ethane to the range between those of ethylene and of carbon dioxide. The transfer of heat in these two gases was compared in a separate series of measurements and since the heat capacities are known, the accommodation coefficient ratios were computed. The results are shown graphically in Fig. 2. As was to be expected from the preceding,

$$\left[\frac{\alpha_{C_2H_4}}{\alpha_{CO_2}}\right]_{\text{wire no. 1}} > \left[\frac{\alpha_{C_2H_4}}{\alpha_{CO_2}}\right]_{\text{wire no. 2}} > 1.$$

It is important, however, that on the platinized wire the ratio of their accommodation coefficients does not deviate from unity by more than 0.7 percent in the temperature range studied and tends toward unity with decreasing temperature. Combining this result with Eq. (4), it is found:

$$0.993 \leq \left[\frac{\alpha_{CO_2}}{\alpha_{C_2H_4}}\right]_{\text{no. 2}} < \left[\frac{\alpha_{C_2D_6}}{\alpha_{C_2H_4}}\right]_{\text{no. 2}} \leq 1$$

$$\leq \left[\frac{\alpha_{C_2D_6}}{\alpha_{CO_2}}\right]_{\text{no. 2}} < \left[\frac{\alpha_{C_2H_4}}{\alpha_{CO_2}}\right]_{\text{no. 2}} \leq 1.007,$$

which is all that is necessary to calculate the

TABLE III. *Relative heat conductivity of* C_2D_6.

Mean of Wire and Bath Temperatures, °K	Y_x on Wire No. 1	No. of Pipettes Admitted*	Mean of Wire and Bath Temperatures, °K	Y_x on Wire No. 2
(a) comparison with ethylene				
331.9	15.07	1	329.7	15.54
331.9	15.00	2	329.7	15.49
328.1	15.09	1	325.9	15.55
328.1	15.05	2	325.9	15.50
295.6	13.75	1	293.5	14.11
295.6	13.90	2	293.5	14.17
215.5	11.39	1	214.0	11.37
215.5	11.39	2	214.0	11.37
(b) comparison with ethane				
336.4	14.71	1	334.3	15.48
336.4	14.72	2	334.3	15.51
331.9	14.66	1	329.7	15.42
331.9	14.63	2	329.7	15.36
		1	329.1	15.40
		2	329.1	15.40
328.1	14.40	1	325.9	15.06
328.1	14.50	2	325.9	15.25
		1	287.6	14.11
		2	287.6	14.13
295.6	13.63	1	293.5	14.12
295.6	13.66	2	293.5	14.09
215.5	11.16	1	214.0	11.14
215.5	11.12	2	214.0	11.11
(c) comparison with carbon dioxide				
336.4	15.96	1	334.3	15.73
336.4	16.01	2	334.3	15.69
		1	329.1	15.42
		2	329.1	15.42
328.1	15.49	1	325.9	15.08
328.1	15.62	2	325.9	15.23
295.6	14.66	1	293.5	14.29
295.6	14.67	2	293.5	14.26
		1	287.6	13.99
		2	287.6	13.92
215.5	11.49	1	214.0	11.29
215.5	11.50	2	214.0	11.28

* Each pipette admits 4.9×10^{-3} mm of gas.

heat capacity of deuterated ethane from the data of Table III.

We believe that the outlined procedure of calculating heat capacities of a gas from the heat conductance measurements alone, even though the accommodation coefficient ratios may not be unity, constitutes an important advance in the usefulness of the "hot wire" method. Indeed, it is normally possible to ascertain whether or not a given gas is better accommodated than another by noting whether Y_x of Eq. (3) decreases or increases when a smooth wire is replaced by one with an unsintered surface, i.e., with a more active surface from the point of view of adsorption. Two assumptions are involved in this determination. One is that on changing from one wire to another the accommodation coefficient of each gas changes in the same direction; the other is that it changes by a greater percentage the smaller its absolute value. The second of these assumptions is more specific, but is quite plausible. In the extreme case of a perfectly accommodated gas the coefficient would not change at all, whereas the accommodation coefficients of very poorly accommodated gases are known to be highly sensitive to the structure of the solid surface. Furthermore this assumption seems to be the only one which satisfactorily correlates measurements made in this laboratory on a number of gases, and is directly confirmed by the fact that correct results are thus obtained for several gases, including C_2D_6. It is expected to hold when wires made of the same material are used for comparison, differences in accommodation coefficients being effected by different methods of preparing the surface. On surfaces of chemically dissimilar materials neither of the above assumptions may hold.

Once two gases with known heat capacities have been found for which Y_x of Eq. (3) show opposite trends when the wire surface is changed, as do $Y_{C_2H_4}$ and Y_{CO_2} of deuterated ethane, the accommodation coefficient of the studied gas can be bracketed, as was done in Eq. (4), because its heat capacity enters as a constant multiplier into all expressions for Y_x. The narrower is the bracket, the more accurate is the calculation of the unknown heat capacity. In the work described here the limits are too widely separated on wire no. 1 to be useful, but on wire no. 2 the uncertainty in locating $\alpha_{C_2D_6}$ with relation to those of the comparison gases is not greater than the other errors of measurement.

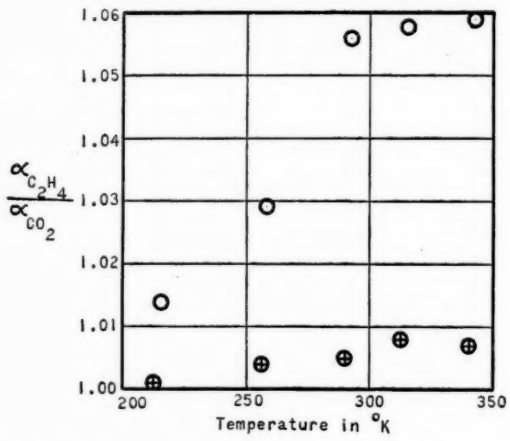

FIG. 2. Accommodation coefficient ratios of C_2H_4 and CO_2. Circles-wire no. 1; crosses-wire no 2.

Table IV presents the calculated heat capacities of C_2D_6 derived from measurements on wire no. 2. Each value is obtained by setting the accommodation coefficient ratio equal to unity; the true values should lie between the limits of each pair of figures obtained using C_2H_4 and CO_2, respectively, for comparison. Below 214°K only ethylene was used as the comparison gas, hence the bracketing method could not be applied. The lower temperature data therefore, are minimum values, but the uncertainty is very small because the accommodation coefficient ratios may be safely assumed equal to unity. The fact that for all three gases of Table III the Y_x's for wires no. 1 and no. 2 approach a common limit as the temperature is lowered is the best evidence in favor of this assumption.

It should perhaps be added that the tests of the effects of the pressure and of the temperature difference, as described for ordinary ethane, were made also for C_2D_6, with equally satisfactory results. C_2H_6 and C_2D_6 were found to be adsorbed in equal amounts at all temperatures, although, as Table III shows, deuterated ethane is markedly less well accommodated at higher temperatures than is C_2H_6.

Discussion

The experimental data now available on the heat capacity of gaseous ethanes are plotted in Fig. 3. The data for C_2D_6 obtained in this investigation by the use of the bracketing method described above are distinguished by horizontal lines showing the range to which the experimental bracketing data limit the heat capacity. A study of the internal consistency of our experimental data and a comparison with the data of the preceding paper indicate that our experimental error, aside from that due to the bracketing procedure, is approximately one percent.

In a preliminary report on part of this work[7] it was pointed out that the heat capacities of gaseous C_2H_6 and C_2D_6 at low temperatures show conclusively that the potential barrier restricting internal rotation in ethane must be of the order of 3000 calories per mole. A restricting potential of the form $V=\frac{1}{2}V_0(1-\cos 3\theta)$ was assumed in arriving at this figure. Although it is not possible at present to deduce accurately both the height and shape of the potential barrier from the available experimental data, it will be shown in the following that the assumption of a cosine type barrier does lead to results consistent with the heat capacity and vibrational spectra of C_2H_6 and C_2D_6.

Without assuming a specific shape for the barrier, the position of the first two torsional oscillation levels in C_2H_6 can be determined directly from heat capacities at low temperatures. They are found to be at 275 and 520 cm^{-1} above the ground level, with an uncertainty of approximately 10 cm^{-1}. The correctness of the vibrational analysis does not affect this determination since the vibrational contribution to the heat capacity is very small at these temperatures. In a portion of Fig. 3 the lower temperature data for C_2H_6 are plotted on a larger scale. The curve drawn shows the heat capacity calculated assuming the first three levels to lie at 275, 520 and 725 cm^{-1} above the ground state, but the contribution from the third level is too small to fix its position accurately. Professor Wilson's calculations show that a cosine shape barrier of 2750 cal./mole (965 cm^{-1}) gives the first three levels[8] at 275, 520 and 726 cm^{-1} above the ground state. This barrier has then been used to calculate[9] the heat capacity of C_2H_6 at higher temperatures using the fundamental frequencies given in Table IV of the following paper.[10] These calculated values are represented by the curve drawn in Fig. 3. The agreement with the experimental results is entirely satisfactory, but it does not show conclusively that the barrier is of a cosine shape because small uncertainties in the vibrational frequencies as well as experimental error in the heat capacity permit appreciable deviations from the theoretical curve. However the relative positions of the first two levels show the same anharmonicity as expected for a cosine potential function. In this connection it is interesting to note that the 520-cm^{-1} level lies

Table IV. *Heat capacity of* C_2D_6.

T°K	C_v	Comparison Gas
334.3	14.72	CO_2
329.7	14.53	C_2H_4
329.1	14.43	CO_2
325.9	14.54	C_2H_4
325.9	14.17	CO_2
293.5	13.30	C_2H_4
293.5	13.15	CO_2
287.6	12.97	CO_2
214.0	10.38	C_2H_4
214.0	10.30	CO_2
157.3	8.46	C_2H_4
100.5	7.14	C_2H_4
99.6	7.13	C_2H_4
94.3	7.03	C_2H_4
93.5	7.03	C_2H_4

[7] G. B. Kistiakowsky, J. R. Lacher and F. Stitt, J. Chem. Phys. **6**, 407 (1938). Since the publication of this note, a paper by K. Schäfer (Zeits. f. physik. Chemie **B40**, 357 (1938)) appeared in which the same conclusion is reached.

[8] Each of these levels is sixfold degenerate and is split into four levels, two of which are twofold degenerate. See E. B. Wilson, Jr., J. Chem. Phys. **6**, 740 (1938). This splitting is only 0.4 cm^{-1} for the first level. The calculated positions of the highest and lowest of these four components for the second and third levels are 523, 517 and 706, 747 cm^{-1} above the ground state.

[9] The heat capacity due to restricted rotation was calculated by direct summation over the energy levels. Below 140°K the result was lower by 0.1 cal. than the values found by graphical interpolation using Table IV of Pitzer (J. Chem. Phys. **5**, 469 (1937)). This difference decreased to about 0.02 cal. above 300°K. In the figure of reference 7, the curves shown for C_2H_6 are therefore somewhat too high, and our experimental points for C_2H_6 and C_2D_6 have more nearly the same abscissa than shown there. The moment of inertia about the threefold axis is taken as 10.59×10^{-40} g cm^2, corresponding to 1.093A for the C−H distance, as found by Ginsburg and Barker from a parallel band in the vibration-rotation spectrum of CH_3D. (J. Chem. Phys. **3**, 668 (1935).)

[10] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

more than two-thirds of the way up the appropriate cosine type barrier.

The curve for C_2D_6 in Fig. 3 represents the calculated[11] heat capacity based on the same cosine potential barrier ($V_0=2750$ cal./mole) as used for C_2H_6 and the fundamental frequencies in Table II of the following paper. At the lower temperatures, where the vibrational contributions are small, the agreement of the calculated curve with the experimental data shows conclusively that the true barrier has a shape very nearly sinusoidal, at least for the lower two-thirds of the barrier.

In the following paper it is concluded that one cannot at present show from the vibrational spectra alone whether the equilibrium configuration of ethane is the staggered (D_{3d}) or the eclipsed (D_{3h}) one. However, as will be discussed in another paper from this laboratory, the interpretation of the heats of hydrogenation of a number of unsaturated cyclic hydrocarbons affords convincing evidence that the more stable configuration is the staggered (D_{3d}) one. If the symmetry is D_{3d} the fundamental frequencies used above are all determined from spectroscopic data. (See the following paper.) The excellent agreement of the calculated with the observed heat capacities of both C_2H_6 and C_2D_6 at higher temperatures is then further evidence that the shape of the restricting potential cannot differ much from the cosine form assumed, for the height of the barrier is fixed by the experimental data on C_2H_6 at lower temperatures and the vibrational heat capacity is determined completely from spectroscopic data.

The entropy of C_2H_6 at 298°K calculated with the same cosine barrier and vibrational frequencies as used above is 54.95 cal./deg.-mole.

[11] The heat capacity due to restricted rotation was obtained by direct summation over the energy levels up to 150°K, and from Table IV, of Pitzer, reference 9, above that temperature. Below 150°K the values differed by those found from Pitzer's table by less than 0.05 cal.

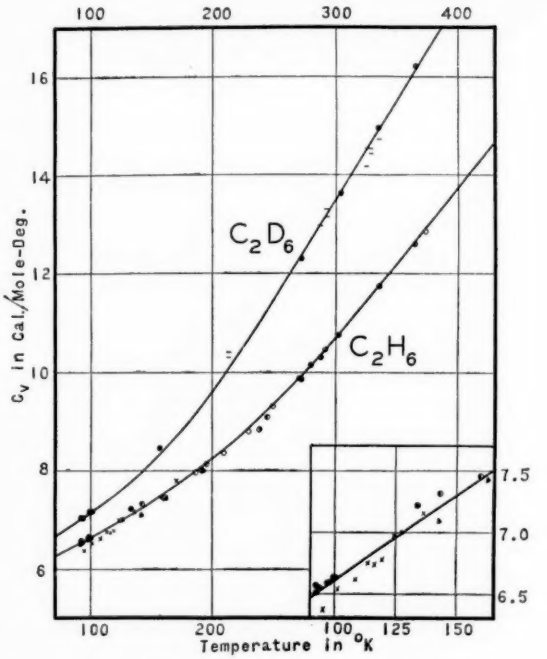

FIG. 3. Heat Capacity of C_2H_6 and C_2D_6. Sources (reference 12) of data: ● This investigation; ⊗ Kistiakowsky and Rice; ○ Eucken and Parts; × Hunsmann; ◐ Eucken and Weigert; ▲ Kistiakowsky and Nazmi; ◑ Heuse.

This agrees well with the third law entropy of 54.85±0.2 cal./deg.-mole found by Witt and Kemp.[13]

In conclusion we wish to thank Professor E. B. Wilson, Jr., for much very helpful discussion in connection with this investigation.

[12] G. B. Kistiakowsky and W. W. Rice, preceding paper; A. Eucken and A. Parts, Zeits. f. physik. Chemie **B20**, 189 (1933); W. Hunsmann, Zeits. f. physik. Chemie **B39**, 23 (1938); A. Eucken and K. Weigert, Zeits. f. physik. Chemie **B23**, 276 (1933); G. B. Kistiakowsky and F. Nazmi, J. Chem. Phys. **6**, 18 (1938); Heuse, Ann. d. Physik **59**, 86 (1919). See also B. H. Sage, D. C. Webster and W. N. Lacey, J. Ind. Eng. Chem. **29**, 658 (1937); A. Eucken and A. Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936); V. R. Thayer and G. Stegeman, J. Phys. Chem. **35**, 1505 (1931).

[13] R. K. Witt and J. D. Kemp, J. Am. Chem. Soc. **59**, 273 (1937).

Infra-Red and Raman Spectra of Polyatomic Molecules. VII. C_2D_6

FRED STITT*
Harvard University, Cambridge, Massachusetts
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The infra-red spectrum of gaseous C_2D_6 has been investigated from 2 to 22μ, and the Raman spectrum of the liquid has been photographed. These data have been analyzed for both the symmetries D_{3d} and D_{3h}. It is concluded that the equilibrium configuration of ethane cannot be reliably determined from the analysis of the data now available on the vibrational spectra of C_2H_6 and C_2D_6. However, the "uncertain frequency" of C_2H_6 is determined by application of the product rule if the symmetry is D_{3d}. A modified valence force type potential function containing interaction terms between the two methyl groups is found to fit the fundamental frequencies of the light and heavy ethanes quite well.

THE preparation of C_2D_6 and the studies of its gaseous heat capacity and vibrational spectrum reported in this and the two preceding papers were undertaken in order to provide further information concerning the potential barrier restricting internal rotation in ethane. In particular it was thought that analysis of the infra-red and Raman spectra of the deuterated ethane might lead to reliable determinations both of the symmetry of the ethane molecule and of the uncertain fundamental frequency of C_2H_6. As in the case of C_2H_6 however, it is found that the equilibrium configuration of ethane cannot be safely determined from the analysis of the C_2D_6 spectrum. The uncertain frequency of C_2H_6 is determined from the analysis of the C_2D_6 spectrum and application of the product rule if the staggered (D_{3d}) configuration is the more stable one.

EXPERIMENTAL

Preparation of C_2D_6

C_2D_6 was prepared by combination of C_2D_2 and D_2 over a platinum catalyst. A number of investigators have studied the catalytic hydrogenation of acetylene since the pioneer work of Sabatier and Senderens.[1] The procedure adopted here was suggested by Professor Kistiakowsky.

The platinum catalyst was prepared by saturating asbestos with platinic chloride solution, drying below 300°C in a slow stream of nitrogen and then in a vacuum, and subsequently passing deuterium over it before using. Preliminary experiments with C_2H_2 and H_2 were made with other similarly prepared catalysts in order to establish the best conditions for the preparation of pure ethane. C_2D_2 was prepared by passing D_2O vapor (>99.6 percent D_2O) over calcium carbide powder which had been dried in vacuum at 500°C. The C_2D_6 was then made in the following manner: Deuterium (dried and free of O_2) from the cathode arm of a U-shaped D_2O electrolyzer was passed over solid C_2D_2 in a U-trap, the temperature of which was controlled so as to give a resulting gas mixture with ratio of D_2 to C_2D_2 of approximately 10 to 1.[2] This mixture was passed over the catalyst maintained at about 100°. C_2D_6 was then trapped out with liquid air. The excess D_2, issuing from a small nozzle, was mixed with dry air and burnt to D_2O by a red hot platinum spiral. Preceding the nozzle was a sintered glass plate which prevented striking back in case an explosive mixture was present. The product was purified by distillation from a bath at −135°C. About six liters of C_2D_6 were prepared in this manner. I wish to thank Professor Kistiakowsky for construction of parts of this apparatus, and Dr. J. R. Lacher for assistance in the preparation of the C_2D_6.

After the C_2D_6 was prepared, a 500-cc sample intended to be C_2D_5H was made by the same deuteriation procedure from a sample supposedly C_2DH. This acetylene was made by passing D_2O vapor over NaC_2H, which in turn was prepared

* National Research Fellow in Chemistry.
[1] P. Sabatier and J.-B. Senderens, Comptes rendus **131**, 40 (1900).
[2] Such a high ratio is not necessary for complete hydrogenation but tends to eliminate polymerized products.

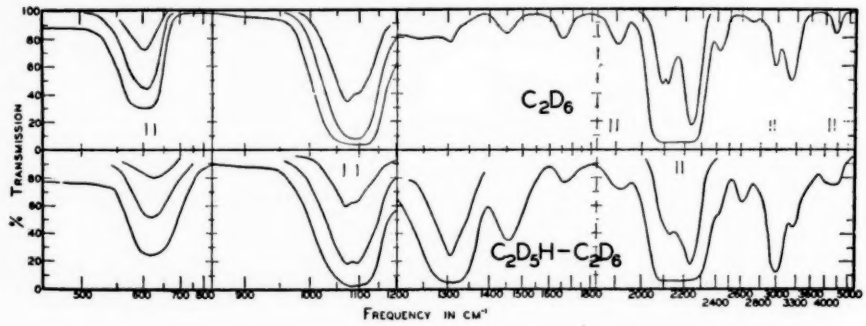

FIG. 1. Absorption spectrum of deuterated ethane. Length of absorption path: 30 cm (except for C_2D_6 in CaF_2 region, where it was 20 cm). Gas pressure in mm Hg: C_2D_6—760, 260, 85 (KBr); 760, 85, 50 (NaCl); 760, 90 (CaF_2). C_2D_6—C_2D_5H—630, 180, 50 (KBr, NaCl); 760, 35 (CaF_2). Effective slit widths are indicated.

by passing C_2H_2 through a solution of sodium in liquid ammonia.[3]

Purity of product

In a distillation of the C_2D_6, comparison of the first and last five-percent portions of the distillate showed little or no difference in vapor pressure, indicating the absence of significant amounts of substances other than ethanes.

I am greatly indebted to Dr. A. O. Nier for mass-spectrographic analyses of a number of samples. In the C_2D_6 he found the ratio of the ion currents for mass numbers 35 and 36 was 0.030 (when corrected for the presence of C^{13}), corresponding to 2.9 percent C_2D_5H. This is to be compared with the expected two percent due to the fact that the heavy water used was not pure D_2O.

The sample supposedly C_2DH was found to be approximately 47.3 percent C_2D_2, 43.0 percent C_2DH, and 9.6 percent C_2H_2. The ethane formed by deuteriation of this acetylene showed a corrected ion current ratio of mass numbers 35 to 36 of 1.26 ± 0.03. This ratio is considerably higher than that (0.91) of the C_2DH to C_2D_2 in the acetylene and indicates considerable exchange on the catalyst. The actual composition is of little importance for this work; it suffices to know that C_2D_6 and C_2D_5H were present in approximately the same proportions, and that an appreciable quantity of $C_2D_4H_2$ was also present.[4]

[3] H. Moissan, Comptes rendus **127**, 911 (1898). See also T. H. Vaughan, G. F. Hennon, R. R. Vogt and J. A. Nieuwland, J. Org. Chem. **2**, 1 (1937).

[4] Reliable analysis for the proportions of other mass numbers than 35 and 36 requires a more extended study than seemed justified for this work. For ethane, only the species C_2D_6 and C_2D_5H correspond, respectively, to mass numbers 36 and 35. For the next lower mass numbers more than one species is involved and a knowledge of the relative abundancies of various mass number radicals produced from the ethanes initially present would be necessary. Under the same conditions of excitation, the relative abundancies of corresponding mass numbers apparently are different for C_2H_6 and C_2D_6.

Infra-red spectrum

The automatic prism spectrometer described in I[5] of this series was used to study the infra-red absorption spectrum from 2 to 22μ of both C_2D_6 and the $C_2D_5H-C_2D_6$ mixture. Three different prisms were employed: CaF_2 from 2 to 8.5μ, NaCl from 6 to 13μ, and KBr from 12.5 to 22μ. The spectrometer was calibrated by observing the position of bands of C_2H_2, C_2H_4, CO_2, C_6H_6, and acetone. The gas was enclosed in either a 20- or a 30-cm long cylindrical cell with either NaCl or KBr windows at pressures from 16 to 760 mm Hg. Blanks were recorded over the entire region.

Figure 1 shows the transmission curves obtained. In regions of strong absorption, curves at some pressures have been omitted. Comparison of the curves for the two samples leaves little doubt as to which bands are due to C_2D_6—those due to C_2D_5H show much greater absorption in the $C_2D_5H-C_2D_6$ mixture. Thus the bands at 1305, 1450 and 2994 cm^{-1} are clearly not due to C_2D_6. All the other bands found in the spectrum shown for C_2D_6 are believed to be due to absorption by C_2D_6 molecules, with the possible exception of the weak band at 2711 cm^{-1}. We shall make no further use of the spectrum of the

[5] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

$C_2D_5H-C_2D_6$ mixture. The frequency of the C_2D_6 bands are recorded in Table III.

The spectrum of ethane containing approximately 95 to 98 percent deuterium (i.e., from about 23 to 11 percent C_2D_5H) has been studied with a rocksalt prism spectrometer by Benedict, Morikawa, Barnes and Taylor.[6] Their results agree satisfactorily with those reported here.

Raman spectrum

The spectrograph and essentially the technique described in II[7] of this series were used in photographing the Raman spectrum of about 10 cc of liquid C_2D_6 at approximately $-80°C$. The iron arc was used as comparison spectrum. The Raman tube employed had two windows with an intervening evacuated space which served to prevent condensation of moisture on the window adjacent to the liquid. Photographs were taken with and without a filter for the removal of the 4047 group as exciting lines. All Raman shifts except the weak one at 1930 cm^{-1} were observed for both 4047 and 4358 as the exciting lines. Polarization measurements were made using the Polaroid method.[8] The Raman data are included in Table III. Microphotometer curves for the polarization measurements are shown in Fig. 2.

The presence of three-percent C_2D_5H is of course not expected to manifest itself so readily in the Raman spectrum as in the infra-red. If

TABLE I. *Designation of the fundamental frequencies of ethane.*

D_{3h}'	FUNDAMENTAL FREQUENCIES	D_{3d}	D_{3h}	SELECTION RULES*
A_1	$\nu(\pi)>\delta(\pi)>\tau(\pi)$	A_{1g}	A_1'	$R(P)$
$\bar{A}_2$	$\bar{\nu}(\pi)>\bar{\delta}(\pi)$	A_{2u}	A_2''	$I(\|\|)$
E	$\nu(\sigma)>\delta(\sigma)>\tau(\sigma)$	E_u	E'	$I(\perp)$, $R(D)$†
$\bar{E}$	$\bar{\nu}(\sigma)>\bar{\delta}(\sigma)>\bar{\tau}(\sigma)$	E_g	E''	$R(D)$
$\bar{A}_1$	ω_i (Restricted Internal Rotation)	A_{1u}	A_1''	

* Symbols: R = Raman active; I = Infra-red active; P = Polarized; D = Depolarized; π, $\|$ = Parallel; σ, $\perp$ = Perpendicular.
† For symmetry D_{3d} this type vibration is not permitted to be Raman active.

[6] W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor, J. Chem. Phys. **5**, 1 (1937).
[7] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).
[8] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938). We are indebted to the Polaroid Corporation for a sample of a recently developed Polaroid which is effective out to much shorter wave-lengths than the older product.

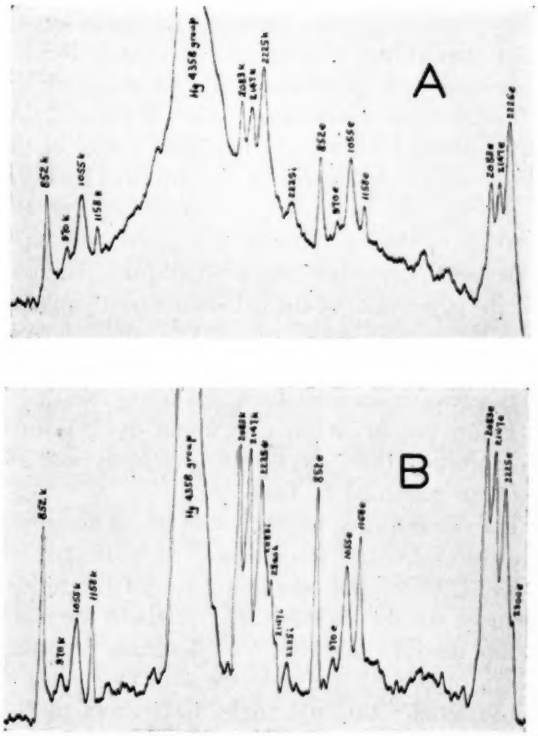

FIG. 2. Microphotometer curves of Raman polarization photographs. A.—Axis of Polaroid parallel to axis of Raman tube. B.—Axis of Polaroid perpendicular to axis of Raman tube. The lines are labeled with the mean frequency values of Table III.

Raman shifts due to C_2D_5H were to appear they are expected to be of the order of three percent as intense as similar shifts due to C_2D_6. Since no Raman shifts in the neighborhood of 3000 or 1500 cm^{-1} were observed, and since the only very weak line (1930 cm^{-1}) observed is not assigned as a fundamental frequency of C_2D_6 and could hardly be a fundamental of C_2D_5H either, it is believed that all the observed Raman lines are due to C_2D_6.

VIBRATIONAL ANALYSIS

Since the symmetry of the equilibrium configuration of ethane is still in doubt,[9] both the D_{3d} (staggered) and the D_{3h} (eclipsed) configurations will be considered in making the vibrational analysis.

There are several guides to aid us in obtaining the fundamental frequencies of C_2D_6 from the

[9] See B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, J. Chem. Phys. **6**, 686 (1938).

vibrational spectrum, namely, (1) the selection rules governing which infra-red and Raman transitions are permitted and the shape of the infra-red band envelopes or state of polarization of the Raman lines; (2) calculated values of the frequencies found by use of the potential function of C_2H_6; (3) the product rule[10] relating the product of the frequencies of a given symmetry type to the corresponding product for C_2H_6; and (4) the agreement of the calculated heat capacity with the experimental values. The selection rules are summarized elsewhere.[11] The fundamental frequencies calculated for C_2D_6 using the three-constant potential function found by Howard[12] to reproduce the C_2H_6 frequencies fairly well are given in column I of Table VI.

For convenience in discussion let us designate the fundamental frequencies as indicated in Table I, where the selection rules for the fundamentals are also included. D_{3h}' refers to the point group used by Howard[12] to describe the symmetry of the ethane molecule with any value of the internal rotational angle. References to D_{3h}' throughout this paper may be interpreted in terms of symmetry D_{3d} or D_{3h} by referring to Table I.

We expect the ν and δ vibrations to be essentially carbon-deuterium stretching and bending frequencies, respectively, hence in the neighborhood of 2100 and 1100 cm^{-1}. We are thus led at once to assign the three strongest regions of absorption in the infra-red spectrum to ν, δ and τ vibrations. Then, in accordance with the selection rules, the band at 601 cm^{-1} must be due to $\tau(\sigma)$. The complex absorption in the 1100 cm^{-1} region is assigned to the overlapping of bands due to $\bar{\delta}(\pi)$ and $\delta(\sigma)$; the band centers have somewhat arbitrarily been chosen as 1072 and 1102 cm^{-1},

TABLE II. *Fundamental frequencies of* C_2D_6.

D'_{3h}, D_{3d}, D_{3h}			
A_1, A_{1g}, A_1':	2115	1158	852
$\bar{A}_2$, A_{2u}, A_2'':	2100	1072	
E, E_u, E' :	2237	1102	601
$\bar{E}$, E_g, E'' :	2225	1055	970
$\bar{A}_1$, A_{1u}, A_1'':	200		

[10] See for example, O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).

[11] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie **B39**, 1 (1938).

[12] J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

TABLE III. *Analysis of the vibrational spectrum of* C_2D_6.

Frequency cm^{-1}	Intensity; Type*	Assignment (See Table I)	Symmetry D_{3d}	Symmetry D_{3h}
Infra-Red				
~ 601	*s*	Fund. $=\tau(\sigma)$	E_u	E'
~1072	*s*	Fund. $=\bar{\delta}(\pi)$	A_{2u}	A_2''
~1102	*s*	Fund. $=\delta(\sigma)$	E_u	E'
1654	*w*	$\tau(\sigma)+\bar{\delta}(\sigma)=1656$	$A_{1u}+A_{2u}+E_u$	$A_1''+A_2''+E''$
1908	*w*	$\tau(\pi)+\bar{\delta}(\pi)=1924$	A_{2u}	A_2''
2088	*s*	Fund. $=\bar{\nu}(\pi)$	A_{2u}	A_2''
2112	*s*			
2237	*s*	Fund. $=\nu(\sigma)$	E_u	E'
2415	*w*	$\bar{\nu}(\sigma)+\omega_i=2425$	E_u	E'
2711?	*w*	$\nu(\pi)+\tau(\sigma)=2716$	E_u	E'
~3200	*m*	$\nu+\delta$		
~4400	*w*	$\nu+\nu$		
Raman (liquid)				
852	*s, sh, P*	Fund. $=\tau(\pi)$	A_{1g}	A_1'
~ 970	*w, bd, D*	Fund. $=\bar{\tau}(\sigma)$	E_g	E''
1055	*m, bd, D*	Fund. $=\bar{\delta}(\sigma)$	E_g	E''
1158	*m, sh, P*	Fund. $=\delta(\pi)$	A_{1g}	A_1'
~1930	*v w*	$2\bar{\tau}(\sigma)=1940$	$A_{1g}+E_g$	$A_1'+E'$
2083	*s, sh, P* Res.	Fund. $=\nu(\pi)$ and $2\bar{\delta}(\sigma)=2110$	A_{1g}	A_1'
2147	*s, sh, P* Res.		$A_{1g}+E_g$	$A_1'+E'$
2225	*s, bd, D*	Fund. $=\bar{\nu}(\sigma)$	E_g	E''
~2300	*w, sh, P*	$2\delta(\pi)=2316$	A_{1g}	A_1'

* Abbreviations: *P* = Polarized; *D* = Depolarized; *s* = strong; *w* = weak; *m* = medium; *sh* = sharp; *bd* = broad; *v* = very; *Res.* = Resonance.

respectively. In the 2100 cm^{-1} region the 2237 cm^{-1} band is assigned to $\nu(\sigma)$ since in both the C_2H_6 and the calculated C_2D_6 frequencies $\nu(\sigma)$ is found to be greater than $\bar{\nu}(\pi)$. The peaks at 2088 and 2112 cm^{-1} are ascribed to the P and R branches of $\bar{\nu}(\pi)$, for which we expect a P–R separation of ~35 cm^{-1} with about one-fifth of the total intensity in the Q branch.[13, 14]

The polarization measurements show at once that the sharp Raman lines at 852, 1158, 2083 and 2147 cm^{-1} are associated with A_1. Accordingly we assign these frequencies, respectively, to $\tau(\pi)$, $\delta(\pi)$, and resonance between $\nu(\pi)$ and[15] 2(1055). The weak polarized line at 2300 cm^{-1} is assigned as 2(1158). The very weak line at 1930 cm^{-1} is assigned as 2(970). The assignment of the other Raman lines may be different according as the symmetry is assumed to be D_{3d} or D_{3h}.

If the symmetry is D_{3d}, the Raman selection rules lead at once to the assignments 2225 cm^{-1} $=\bar{\nu}(\sigma)$, $1055=\bar{\delta}(\sigma)$, and $970=\bar{\tau}(\sigma)$.

If the symmetry is D_{3h}, both the E and the $\bar{E}$ fundamental vibrations are permitted to appear

[13] See S. Gerhard and D. M. Dennison, Phys. Rev. **47**, 197 (1933).

[14] The Q branch was not observed probably because it was necessary to use too large a slit width. If, however, the peaks at 2088 and 2112 cm^{-1} represent two Q branches, resonance between $\bar{\nu}(\pi)$ and 1102+970 must be responsible.

[15] Perhaps 2(1072) instead of 2(1055).

in the Raman spectrum. Since the values of the E frequencies have already been determined from the infra-red spectrum, we can at once assign 970 $cm^{-1} = \bar{\tau}(\sigma)$. However 1055 cm^{-1} may be either $\bar{\delta}(\sigma)$ or $\delta(\sigma)$, and 2225 cm^{-1} may be either $\bar{\nu}(\sigma)$ or $\nu(\sigma)$, the latter alternatives corresponding to 1072 and 2237 cm^{-1} found for these frequencies in the gas phase from the infra-red spectrum.

The remaining infra-red bands are readily assigned. For each of the bands 1654, 1908, 2415 and 2711 cm^{-1}, the assignment given in Table III seems to be the only reasonable one for symmetry D_{3d}; for D_{3h} these same numerical assignments seem to be the best, although there are other possibilities which cannot at present be excluded.

The set of fundamental frequencies found for C_2D_6 is summarized in Table II. The analysis of the complete vibrational spectrum is given in Table III. If ethane has the staggered (D_{3d}) configuration, we are definitely led to the assignments of Tables II and III. If, however, the eclipsed (D_{3h}) configuration is the correct one, there are a number of other possible assignments mentioned above and not indicated in these tables. The $\bar{A}_1$ frequency of Table II represents the height above the ground state of the first torsion oscillation level as calculated on the basis of a cosine type potential barrier of 2750 cal./mole.[16]

The frequencies of Table II are seen to be in satisfactory agreement with those calculated with the three constant potential function of C_2H_6. (See column I of Table VI.) In the preceding paper[16] it is shown that the heat capacity calculated with the aid of the frequencies of Table II is in excellent agreement with the observed values. That this set of fundamental frequencies also satisfies the product rule will be shown in the next section.

TABLE IV. *Fundamental frequencies of* C_2H_6.

D'_{3h}, D_{3d}, D_{3h}			
A_1, A_{1g}, A_1' :	2925	1375	993
$\bar{A}_2$, A_{2u}, A_2'':	2925	1380	
E, E_u, E' :	2980	1465	827
$\bar{E}$, E_g, E'' :	2960	1460	1170
$\bar{A}_1$, A_{1u}, A_1'':	275		

[16] See the preceding paper: G. B. Kistiakowsky, J. R. Lacher and F. Stitt, J. Chem. Phys. **7**, 289 (1939).

APPLICATION OF THE PRODUCT RULE AND THE UNCERTAIN FREQUENCY OF C_2H_6

It will be necessary in applying the product rule and in discussing the vibrational potential function of the ethane molecule to make use of the fundamental frequencies of C_2H_6. The analysis of the vibrational spectrum of ordinary ethane is discussed in Appendix I. There it is concluded that all of the fundamental frequencies except ω_i and $\bar{\tau}(\sigma)$ are determined from the spectroscopic data to have very nearly the values given in Table IV, regardless of which is the correct equilibrium configuration. ω_i is determined by the low temperature heat capacity.[16] The determination of $\bar{\tau}(\sigma)$ will be discussed below.

The ratios of the products of the fundamental frequencies of each symmetry type of C_2H_6 to the corresponding products for C_2D_6 are tabulated in Table V. The "theoretical" ratios of Table V are those found by application of the product rule,[10, 17] while the "observed" ratios were calculated from the frequencies of Tables II and IV. All of the frequencies of the A_1, $\bar{A}_2$ and E symmetry types for both C_2H_6 and C_2D_6 are determined from spectroscopic data, so that the agreement between the "theoretical" and "observed" ratios in these cases confirms the correctness of these assignments.

The product rule is based on two assumptions, namely that both isotopic molecules have the same vibrational potential function and that this function is of a quadratic type. The latter assumption is known to be rigorously true only for infinitesimal amplitudes of vibration. We expect the anharmonic effects to be more marked in C_2H_6 than in C_2D_6 because of the larger

TABLE V. *Application of the product rule to* C_2H_6 and C_2D_6.

D'_{3h}, D'_d, D_{3h}	PRODUCT RATIO THEOR.	OBS.
A_1, A_{1g}, A_1' :	2.00	1.91
$\bar{A}_2$, A_{2u}, A_2'':	1.82	1.79
E, E_u, E' :	2.58	2.44
$\bar{E}$, E_g, E'' :	2.35	(2.22)
$\bar{A}_1$, A_{1u}, A_1'':	1.41	(1.39)

[17] The moments of inertia used were those calculated assuming tetrahedral angles, a C−C distance of 1.55A, and a C−H distance of 1.093A. The latter distance is that found by Ginsburg and Barker from a parallel type band of CH_3D (J. Chem. Phys. **3**, 668 (1935)).

TABLE VI. *Fundamental frequencies of ethane calculated with various potential functions.**

	OBSERVED	I†	II	III
C_2H_6				
	993	990	1015	1010
A_1	1375	1565	1350	1375
	2925	2900	2900	2900
	1380	1375	1400	1390
$\tilde{A}_2$	2925	2890	2895	2895
	827	840	835	830
E	1465	1480	1485	1495
	2980	3010	3010	3010
	1170	1010	1010	1200
$\tilde{E}$	1460	1460	1465	1445
	2960	3015	3015	3020
C_2D_6				
	852	760	825	845
A_1	1158	1400	1150	1140
	2115	2115	2095	2100
	1072	1050	1070	1060
$\tilde{A}_2$	2100	2080	2080	2085
	601	605	600	600
E	1102	1070	1070	1080
	2237	2240	2240	2240
	970	795	795	930
$\tilde{E}$	1055	1055	1050	1055
	2225	2255	2255	2260

* Force constants in 10^5 dynes/cm. I: $K_H=4.79$, $K_C=5.62$, $K_\alpha=K_\beta=0.46$. II: $K_H=4.79$, $K_C=4.60$, $K_{C\gamma}=-0.47$, $K_\alpha=0.46$, $K_\beta=0.46$, $K_{\alpha\beta}=-0.015$. III: $K_H=4.79$, $K_C=4.50$, $K_{C\gamma}=-0.50$, $K_\alpha=0.46$, $K_\beta=0.55$, $K_{\alpha\beta}=0.02$. D_{3d}: $k_{\beta\beta}=-0.18$, $k_{\beta\alpha}=-0.11$, $k_{\beta\alpha}=-0.05$. D_{3h}: $k_{\beta\beta}=-0.18$, $k_{\beta\alpha}=-0.06$.

† The values here for C_2H_6 are slightly lower than those given by Howard, as he used a conversion factor in error by 0.4 percent. The calculated value of $\nu_{10}=\bar{\delta}(\sigma)$ reported before should have been 1465.

vibrational amplitudes of the hydrogen atoms of the former. It is to be noted then that the "observed" ratios differ from the "theoretical" ones in the direction anticipated due to anharmonicity. However the "observed" product ratios are at most two percent less than the "theoretical" ones for methane, ethylene and acetylene. The larger differences found in Table V are probably due to experimental uncertainty as to the exact values of the frequencies.

If the symmetry is D_{3d}, all[18] the fundamental frequencies of both ethanes are found from their vibrational spectra except $\bar{\tau}(\sigma)$ of C_2H_6. We can then determine this, the so-called uncertain frequency of ethane, by application of the product rule. The value of 1170 cm^{-1} given for this frequency in Table IV was thus determined, arbitrarily assuming the "observed" product ratio to be the same fraction of the "theoretical" as was found to be the case for the E type vibrations. We have then determined all the fundamental frequencies of both isotopic molecules (if they possess the symmetry D_{3d}) from spectroscopic data and use of the product rule.

If the symmetry is D_{3h}, not only $\bar{\tau}(\sigma)$ of C_2H_6, but also $\bar{\nu}(\sigma)$ and $\bar{\delta}(\sigma)$ of C_2D_6 are not definitely determined from the vibrational spectra. In this case $\bar{\tau}(\sigma)$ for light ethane and $\bar{\delta}(\sigma)$ for heavy ethane may be determined from the heat capacity data to have approximately the values given them in Tables II and IV if one assumes a cosine type potential barrier restricting internal rotation.

THE STABLE EQUILIBRIUM CONFIGURATION OF ETHANE

Karweil and Schäfer[19] concluded from their analysis of the C_2H_6 vibrational spectrum that the stable equilibrium configuration of ethane is the eclipsed (D_{3h}) one. Crawford, Avery and Linnett[20] have pointed out, however, that the data so far available on the vibrational spectrum of C_2H_6 can be interpreted on the basis of either the D_{3d} or the D_{3h} configuration. (See also Appendix I.) Likewise the C_2D_6 spectrum may be analyzed on either basis. We must therefore conclude that the equilibrium configuration of ethane cannot be reliably determined from the available spectroscopic data.[21]

THE VIBRATIONAL POTENTIAL FUNCTION OF ETHANE

The calculation of the fundamental frequencies of vibration of polyatomic molecules on the basis of simplified quadratic potential functions has met with rather limited success.[22] The most promising procedure at present seems to be to

[18] This does not include the restricted internal rotation frequency ω_i.

[19] J. Karweil and K. Schäfer, Zeits. f. physik. Chemie **B40**, 382 (1938).

[20] B. L. Crawford, Jr., W. H. Avery and J. W. Linnett, J. Phys. Chem. **6**, 682 (1938).

[21] Professor Kistiakowsky informs me that the interpretation of the heats of hydrogenation of a number of unsaturated cyclic hydrocarbons indicates that the staggered (D_{3d}) configuration is the more stable one.

[22] See for example, J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934).

use a valence force type potential function and include those cross terms which physically may be expected to be large for the case in question.[23] Considerable success has attended the retention of force constants thus found relating to a portion of one molecule when applied to other molecules containing the same grouping.[23] More complicated potential functions for ethane than that used by Howard[12] are considered here primarily because of the possibility of obtaining results which may be of use in treating other hydrocarbon molecules.

Howard[12] used the following valence force type potential function

$$2V=K_H\sum_{i=1}^{3}(\Delta r_i'^2+\Delta r_i''^2)+K_C(\Delta R)^2$$
$$+K_\beta r_0^2\sum_{i=1}^{3}(\Delta\beta_i'^2+\Delta\beta_i''^2)$$
$$+K_\alpha r_0^2\sum_{i>j=1}^{3}(\Delta\alpha_{ij}'^2+\Delta\alpha_{ij}''^2) \quad \text{(I)}$$

with K_α and K_β assumed to be the same. Here the single and double primes refer to different methyl groups and i, j are subscripts labeling the three H atoms of a methyl group R is the $C'-C''$ distance; r' is the $C'-H'$ distance; β_i' is the $H_i'-C'-C''$ angle; α_{ij}' is the $H_i'-C'-H_j'$ angle; Δ refers to the change in the following symbol from its equilibrium value. The frequencies for both light and heavy ethane calculated for this function with the values of the three force constants given by Howard are listed in column I of Table VI. The agreement of these calculated frequencies with the observed ones is quite good for the $\bar{A}_2$ and E vibrations, but is poor for $\delta(\pi)$ and $\bar{\tau}(\sigma)$ in both ethanes and for $\tau(\pi)$ in C_2D_6.

It is interesting to note the effect of the substitution of D for H atoms on the A_1 frequencies. The fact that the observed values of $\nu(\pi)$ and $\delta(\pi)$ of C_2H_6 are approximately the same as $\bar{\nu}(\pi)$ and $\bar{\delta}(\pi)$, respectively, indicates that the A_1 normal modes of vibration are approximately pure hydrogen stretching, pure hydrogen bending, and pure carbon-carbon stretching motions. If these same motions were also approximately the normal modes for C_2D_6, we should expect $\nu(\pi)$, $\delta(\pi)$, and $\tau(\pi)$ to decrease by approximately the factors 1.41, 1.41 and 1.10, respectively, on passing from the light to the heavy compound. These observed factors are respectively 1.38, 1.19 and 1.16, indicating that the hydrogen bending and carbon-carbon stretching motions are rather strongly coupled in C_2D_6. The three constant potential function exaggerates this effect.

The existence of the barrier to internal rotation in ethane indicates that there is an interaction between the two methyl groups, but little is known about the absolute magnitude of this interaction for the equilibrium configuration. It was therefore thought desirable to see if a more complicated potential function still involving no interaction terms between the two methyl groups could be found which would remedy the defects of (I). The fact that the frequencies for either the two degenerate or the two nondegenerate types of vibration are essentially the same in both C_2H_6 and C_2D_6 shows that the hydrogen stretching motion is not much coupled with other types of motion; accordingly no cross terms involving Δr have been included in the potential functions to be discussed. In column II of Table VI are shown the calculated frequencies for the function

$$2V=(I)+K_{C\beta}r_0(\Delta R)\sum_{i=1}^{3}(\Delta\beta_i'+\Delta\beta_i'')$$
$$+K_{C\alpha}r_0(\Delta R)\sum_{i>j=1}^{3}(\Delta\alpha_{ij}'+\Delta\alpha_{ij}'')$$
$$+K_{\alpha\beta}r_0^2\sum_{i=1}^{3}\{\Delta\beta_i'(\Delta\alpha'_{i,\,i+1}+\Delta\alpha'_{i,\,i-1})$$
$$+\Delta\beta_i''(\Delta\alpha''_{i,\,i+1}+\Delta\alpha''_{i,\,i-1})\} \quad \text{(II)}$$

with K_α and K_β not assumed equal. This function has six independent constants since $K_{c\alpha}$ and $K_{c\beta}$ appear in the equations only as the combination $K_{c\gamma}=K_{c\alpha}-K_{c\beta}$. The constants were chosen so as to give the best fit with the observed A_1, $\bar{A}_2$ and E frequencies. Equations for the frequencies are discussed in Appendix II. The introduction of the cross terms involving ΔR has improved the calculated A frequencies. However, the only reasonable values of K_α, K_β and $K_{\alpha\beta}$ which

[23] See H. W. Thompson and J. W. Linnett, J. Chem. Soc. pp. 1376, 1384 (1937).

give agreement with the observed E frequencies are such that K_α and K_β are nearly equal and $K_{\alpha\beta}$ is nearly zero; in other words the potential function (II) essentially reduces to (I) so far as the degenerate vibrations are concerned.[24] This is not surprising in view of how well (I) fits the observed E frequencies. For (II) the only calculated frequency differing by much more than three percent with the observed value is $\bar{\tau}(\sigma)$. One must introduce interaction terms between the two methyl groups to remove this discrepancy.

The cross terms which are expected to be important for the interaction between the two methyl groups are somewhat different for the D_{3d} and the D_{3h} configurations. In the following H_i' and H_i'' are symmetrically located with respect to the center of symmetry for D_{3d}, and with respect to the plane (σ_h) of symmetry perpendicular to the threefold axis for D_{3h}. For the D_{3d} configuration, the following potential function has been considered:

$$2V=(II)+k_{\beta\beta}r_0^2\sum_{i=1}^{3}\{\Delta\beta_i'(\Delta\beta''_{i+1}+\Delta\beta''_{i-1})\}$$
$$+k_{\beta\alpha}r_0^2\sum_{i=1}^{3}(\Delta\beta_i'\Delta\alpha''_{i+1,\,i-1}+\Delta\beta_i''\Delta\alpha'_{i+1,\,i-1})$$
$$+k_{\beta\alpha}'r_0^2\sum_{i=1}^{3}\{\Delta\beta_i'(\Delta\alpha''_{i,\,i+1}+\Delta\alpha''_{i,\,i-1})$$
$$+\Delta\beta_i''(\Delta\alpha'_{i,\,i+1}+\Delta\alpha'_{i,\,i+1})\}. \quad \text{(IIId)}$$

The potential function corresponding to approximately the same physical interactions for the D_{3h} configuration involves one less force constant:

$$2V=(II)+k_{\beta\beta}r_0^2\sum_{i=1}^{3}(\Delta\beta_i'\Delta\beta_i'')$$
$$+k_{\beta\alpha}r_0^2\sum_{i=1}^{3}\{\Delta\beta_i'(\Delta\alpha''_{i,\,i+1}+\Delta\alpha''_{i,\,i-1})$$
$$+\Delta\beta_i''(\Delta\alpha'_{i,\,i+1}+\Delta\alpha'_{i,\,i-1})\}. \quad \text{(IIIh)}$$

The best fit with the observed frequencies for the functions (IIId) and (IIIh) led to exactly the same equations and equivalent sets of force constants. The calculated frequencies and the force constants used for (IIId) and (IIIh) are both found under (III) in Table VI. The equations are discussed in Appendix II. It is seen that the inclusion of these cross terms involving both methyl groups has led to higher calculated values of $\bar{\tau}(\sigma)$. All of the cross terms introduced in (IIId) or (IIIh) must be included in order to get the higher calculated value of $\bar{\tau}(\sigma)$ without destroying the agreement of the calculated and observed A frequencies.

In conclusion I wish to thank Professor E. B. Wilson, Jr., for valuable suggestions and discussions relating to this problem.

Note added in proof.—Professor Barker has very recently suggested[25] a somewhat different assignment than that made above for the hydrogen bending fundamentals of C_2H_6. Although the available evidence does not permit assignment of these fundamentals with certainty, there are certain objections to his proposed assignment. (1) According to his assignment the infra-red band at 2755 cm^{-1} should be a $\perp$-type band, whereas it appears to be clearly a $\|$-type band with the expected separation of the P and R branches. (2) In accordance with the selection rules the symmetry of C_2H_6 must be D_{3h} if the 2755 cm^{-1} band is due to a first overtone, whereas the staggered (D_{3d}) configuration seems to be the more stable one.[21] (3) It is difficult to account for a second $\|$-type band in the 2900 cm^{-1} region on the basis of his assignment. With the fundamentals of Table IV this is accounted for by a resonance assignment very similar to that made in the case of the methyl halides.[26]

The following points should be considered in connection with Professor Barker's reasons for believing the assignment $\delta(\pi)=1375$ implausible. (1) The comparison of the 1623 cm^{-1} frequency of C_2H_4 with the 1444 cm^{-1} frequency seems irrelevant since the former is associated with a motion which is primarily C=C stretching.[23] Insofar as such a comparison is justified, it is the 1342 cm^{-1} frequency which should be compared with the 1444 one. (2) The absence of a Raman line at 1375 cm^{-1} in C_2H_6 is not particularly surprising in view of the fact that Raman lines associated with symmetrical hydrogen bending in CH_3NH_2, CH_3OH, CH_3SH, and CH_3Cl are all

[24] K_c and $K_{c\gamma}$ are not involved in the E and $\bar{E}$ equations.

[25] E. F. Barker, J. Chem. Phys. **7**, 277 (1939).

[26] A. Adel and E. F. Barker, J. Chem. Phys. **2**, 627 (1934).

very weak.[27] In CH_3D and CD_3H such lines have not been observed.[28] Likewise in CH_4 and CD_4 the doubly degenerate, Raman active, hydrogen bending frequency is not observed as a fundamental in the Raman spectrum. Although the reasons for such Raman intensity relations are not clear, it may well be that it is only when the symmetrical hydrogen bending motion is appreciably coupled with another type of motion in which the polarizability changes markedly that the fundamental frequency associated with the former appears with appreciable intensity in the Raman spectrum. Thus in C_2H_4, coupling of symmetrical hydrogen bending with C=C stretching motion may account for the strength of the 1342 cm^{-1} Raman line. Similarly in C_2D_6 coupling with the C−C stretching may be responsible for the strength of the 1158 cm^{-1} Raman line, while in C_2H_6 this coupling is so small that a Raman line at 1375 cm^{-1} is not observed.

Appendix I

Analysis of the C_2H_6 vibrational spectrum

The recent analyses of the C_2H_6 vibrational spectrum by Crawford, Avery and Linnett[20] and by Karweil and Schäfer[19] are quite different. The use of the set of fundamental frequencies given in Table IV therefore requires some further discussion.

The experimental data on the C_2H_6 spectrum are summarized elsewhere.[20, 19] The ν and δ frequencies are expected to be in the neighborhood of 3000 and 1500 cm^{-1}, respectively, so we at once identify the three strongest regions of absorption with ν, δ and τ vibrations. Levin and Meyer studied these regions under high dispersion, and their results are therefore considered more reliable than the later lower dispersion studies of these regions. Then, in accordance with the selection rules, we make the following assignments. The $\perp$-type band with center at 827 cm^{-1} is due to $\tau(\sigma)$. The 1500 cm^{-1} region contains a $\perp$-type band with center at ~1465 and a $\parallel$-type band with Q branch at 1380; these frequencies are then assigned as $\delta(\sigma)$ and $\bar{\delta}(\pi)$, respectively. In the records of Levin and Meyer there is no evidence of a second $\perp$-type band at 1495 as reported by Bartholomé and Sachsse. The higher dispersion work also suggests that the band reported by Crawford, Avery and Linnett at 1414 is due to the R branch of $\bar{\delta}(\pi)$, for which we expect[13] a $P-R$ separation of 40 cm^{-1}. In the 3000 cm^{-1} region the $\perp$-band with center at ~2980 must be $\nu(\sigma)$, and the two $\parallel$-bands with Q branches at 2895 and 2955 are assigned to resonance between $\bar{\nu}(\pi)$ and $\delta(\sigma)+\bar{\delta}(\sigma)$, the latter being apparently the only simple possibility permitted by the selection rules. This last assignment fixes $\bar{\delta}(\sigma)$ as ~1460. In Levin and Meyer's study the presence of methane as impurity was believed to have caused the peak near 3015 cm^{-1}. The lower dispersion work of Bartholomé and Karweil showed a peak at 3007; if this is due to ethane its origin is not certain.

The Raman polarization measurements show at once that $\tau(\pi)=993$ and $\nu(\pi)$ is ~2925. The remaining A_1 frequency is fixed as ~1375 by assigning the $\parallel$-band at 2755 to $\delta(\pi)+\bar{\delta}(\pi)$. This is the only simple assignment permitted by the selection rules, and seems much more plausible than the complicated assignment of Karweil and Schäfer. The 1344 Raman line of Goubeau and Karweil is probably due to C_2H_4, as it was not observed by Glockler and Renfrew in ethane made from EtMgBr. $\bar{\nu}(\sigma)$ is expected to be not very different from $\nu(\sigma)$. It is very likely responsible for one of the weak gas Raman lines (probably 2963). The assignment[29] of the $\perp$-band in the 2675 cm^{-1} region as $\bar{\nu}(\sigma)-\omega_i$ confirms the determination of $\bar{\nu}(\sigma)$ as ~2960.

We have thus determined all of the fundamental frequencies except $\bar{\tau}(\sigma)$ and ω_i, regardless of which is the stable equilibrium configuration of ethane. The resulting set of frequencies (see Table IV) is essentially the same as that of Crawford, Avery and Linnett, except for somewhat different values for $\bar{\tau}(\sigma)$ and ω_i, which have already been discussed.

If the symmetry of ethane is D_{3d} the selection rules are somewhat more stringent than for symmetry D_{3h}. A tentative analysis of the entire C_2H_6 vibrational spectrum on the basis of essentially the frequencies of Table IV has been given by Crawford, Avery and Linnett for either

[27] See summary of data by J. Wagner, Zeits. f. physik. Chemie **B40**, 36 (1938).

[28] G. E. MacWood and H. C. Urey, J. Chem. Phys. **4**, 403 (1936).

[29] A less likely, possible assignment is $\sim 1465+\bar{\tau}(\sigma)$.

configuration. We shall discuss briefly to what extent their analysis may be considered final. The three strongest absorption regions in the infra-red and the bands at 2755 and 2675 have already been discussed. The assignments given for the 1740, 2230, 2300 and 2350 bands are the only simple ones in accordance with the selection rules for D_{3d}; for D_{3h} these same assignments are all permitted, in addition to the other possibilities listed for 2230 and 2300. The assignments of the complicated bands above 3000 cm^{-1} are very doubtful. In the Raman spectrum the assignments of the 975, 993, 2744, 2778 and 2963 lines are probably correct. The 2940 line may be the E component of the overtone ($2\delta(\sigma)$ or $2\bar{\delta}(\sigma)$) in resonance with $\nu(\pi)$. If the symmetry is D_{3d}, 1463 is doubtless $\bar{\delta}(\sigma)$. The assignments of the doubtful Raman lines at 813 and 620 cm^{-1} are very uncertain.

Karweil and Schäfer concluded that the stable equilibrium configuration of ethane is the eclipsed (D_{3h}) one because they could find no satisfactory assignment for the complicated absorption band in the 2200 to 2250 cm^{-1} region except $2\bar{\tau}(\sigma)$, which is permitted to appear by the D_{3h} but not the D_{3d} selection rules. This seems to the author insufficient evidence to justify such an important conclusion.

Appendix II

Equations for the vibrational frequencies

Potential function (II).—The equations relating the frequencies and the force constants for potential function (II) are the same as those for (I) except for addition of more terms. The equations for (I) have already been given by Howard[12] for the A_1, $\bar{A}_2$ and E vibrations. In the following the symbols have the same meaning[30] as in Howard's paper, except for the force constants K.

A_1 vibrations: To the left-hand side of Eq. (12) of Howard add the terms

$$-2\mu CK_4\omega^2+(2\mu CK_1K_4-CK_4^2)\omega+CK_1K_4^2,$$

where the constants K are the following:

$$K_1=K_H;\quad K_2'=K_\gamma=K_\beta+ZK_\alpha-2K_{\alpha\beta}\sqrt{Z};$$

$$K_3'=\tfrac{2}{3}CK_C;\quad K_4=K_{C\gamma};$$

and $C=3m/M$.

$\bar{A}_2$ vibrations: Set $K_3=K_4=0$ in A_1 equation.

E vibrations: To the left-hand side of Eq. (13) of Howard add the terms

$$-\tau(E-3)K_5\omega^2$$

$$-\left(2\tau K_1K_5+\frac{4F+G(1+\tau^2)}{2L}K_5^2\right)\omega+FK_1K_5^2,$$

where the constants K are the following:

$$K_1=K_H;\quad K_2=K_\beta;\quad K_2''=Y^2K_\alpha;\quad K_5=\tfrac{1}{2}YK_{\alpha\beta};$$

$$Y^2=\frac{3}{4-3\mu^2}.$$

$\bar{E}$ vibrations:

$$\omega^3-\omega^2\left\{\frac{L}{2}K_1+\frac{K_2}{2L}\left(\frac{L}{d}+J^2+\frac{U^2}{N}\right)\right.$$

$$\left.+\frac{K_2''}{2L}(P^2+4N)+\frac{K_5}{L}(PJ+2U)\right\}$$

$$+\omega\left\{\left(\frac{U^2}{N}+\frac{L}{d}\right)\frac{K_1K_2}{4}+UK_1K_5+NK_1K_2''\right.$$

$$+\frac{1}{4}\left[\frac{1}{L^2N}(2NJ-PU)^2+\frac{1}{Ld}(4N+P^2)\right]$$

$$\left.\times[K_2K_2''-K_5^2]\right\}-\frac{N}{2d}(K_1K_2K_2''-K_1K_5^2)=0,$$

where the constants K have the same meaning as above, and

$$P=\mu^3C;\quad U=-2\tau+\frac{2Pr_0}{\mu R_0};\quad J=\mu\tau C+2\mu C\frac{r_0}{R_0};$$

$$d=\frac{Nf}{2FH^2};\quad f=1+\frac{CNr_0^2}{2F^2c_0^2};$$

$$H=1+\frac{2r_0}{R_0}\left(\frac{\tau C}{F}+\frac{CNr_0}{2F^2c_0}\right)$$

and c_0 is the equilibrium distance from the center of gravity of the whole molecule to the center of gravity of one of the methyl groups. The $\bar{E}$ equation for (I) is obtained from this by setting $K_5=0$.

[30] $\tau=\cos(\pi-\beta^\circ)$ rather than $\cos\beta^\circ$ as stated before. In the calculations for Table VI it was assumed that α° and β° have the regular tetrahedral values.

Potential function (III).—The equations for (II) apply also for (IIId) and (IIIh), except that the constants K now have different meanings. K_1, K_2'', K_3' and K_4 are the same as above. Where there is a choice of sign in the following equations, the upper sign is for the first and the lower sign for the second of the two symmetry types whose symbols precede the equation.

(IIId):

$$A_{1g},\ A_{2u}: K_2' = K_\beta \pm k_{\beta\beta} + ZK_\alpha - 2(K_{\alpha\beta} \pm \tfrac{1}{2}k_{\beta\alpha} \pm k_{\beta\alpha}')\sqrt{Z}.$$

$$E_u,\ E_g: K_2 = K_\beta \pm \tfrac{1}{2}k_{\beta\beta};\ K_5 = \tfrac{1}{2}Y(K_{\alpha\beta} \pm k_{\beta\alpha} \mp k_{\beta\alpha}').$$

(IIIh):

$$A_1',\ A_2'': K_2' = K_\beta \pm \tfrac{1}{2}k_{\beta\beta} + ZK_\alpha - 2(K_{\alpha\beta} \pm k_{\beta\alpha})\sqrt{Z}.$$

$$E',\ E'': K_2 = K_\beta \pm \tfrac{1}{2}k_{\beta\beta};\ K_5 = \tfrac{1}{2}Y(K_{\alpha\beta} \pm k_{\beta\alpha}).$$

Further details.—The symmetry coordinates used by Howard were also used in this work. The labor involved in the preliminary fitting of the potential function to the observed frequencies was greatly diminished by reducing the cubic equations to quadratics through neglect of the nondiagonal elements of the secular determinant in the row and column associated with the "hydrogen stretching" symmetry coordinate. The roots of the quadratics were usually within one percent of the corresponding roots of the cubic equations.

For finding the approximate solutions of complete cubic equations, the graphical method of Massau as simplified by d'Ocagne[31] was found very useful.

[31] M. d'Ocagne, *Traité de Nomographie* (Gauthier-Villars, Paris, 1921), p. 385.

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Infra-Red and Raman Spectra of Polyatomic Molecules. VIII. Dimethyl Ether

BRYCE L. CRAWFORD, JR.* AND LOIS JOYCE†
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

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The infra-red spectrum of dimethyl ether has been studied from 2.5 to 22.5μ, and the available Raman data correlated with it. A tentative vibrational analysis is given.

IN CONNECTION with the research program on potentials restricting internal rotations of methyl groups, now in progress in this laboratory,[1] we have examined the infra-red spectrum of dimethyl ether between 2.5 and 22.5μ. We present here the infra-red data, together with an evaluation of the available Raman data and a tentative assignment of the vibrational frequencies.

EXPERIMENTAL

The material used was obtained from the Ohio Chemical Company; its purity was listed as 99.95 percent. It was used without further purification. The spectrometer has been previously described;[2] fluorite, rocksalt and KBr prisms were used in the appropriate regions. The absorption curve is given in Fig. 1; the frequencies of the absorption maxima are tabulated in Table I. The very weak shoulders found at 1102 and 2325 cm^{-1} are somewhat doubtful. The indications of the 1102 cm^{-1} shoulder are especially weak; however, these indications appear on every record of this region. A strong band not far below 450 cm^{-1} is shown quite clearly by the absorption curve. It is unfortunate that we were not able to go out to longer wave-lengths and find the center of this band.

The accuracy with which the frequencies were determined is indicated by the effective slit-widths given at appropriate points in Fig. 1.

* National Research Fellow in Chemistry.
† Present address, University of Illinois, Urbana, Illinois.
[1] B. L. Crawford, Jr., J. W. Linnett and W. H. Avery, J. Chem. Phys. **6**, 682 (1938); G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, *ibid.* **6**, 900 (1938); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *ibid.* **7**, 289 (1939); F. Stitt, *ibid.* **7**, 297 (1939).

[2] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

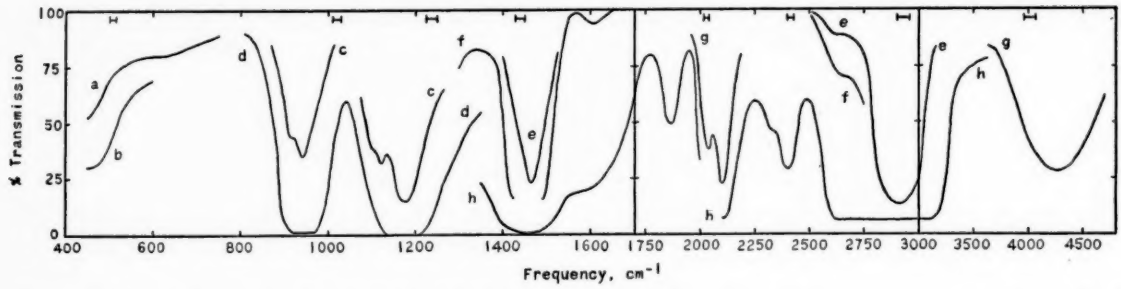

FIG. 1. Infra-red absorption of methyl ether. Path length, 30 cm. KBr prism: *a*, 208 mm pressure; *b*, 730 mm. Rock-salt prism: *c*, 15 mm; *d*, 208 mm. Fluorite prism: *e*, 34 mm; *f*, 117 mm; *g*, 254 mm; *h*, 760 mm. Effective slit-widths are shown near the top of the graph.

DISCUSSION

Previous work

The infra-red spectrum of dimethyl ether apparently has been studied previously only by Coblentz.[3] With due allowance for impurities contained in his sample (especially butane), his results for the stronger bands are in good agreement with ours.

The Raman spectrum has been studied several times.[4–8] The results of the investigations are tabulated in Table II. It will be seen that the agreement on the stronger lines is satisfactory. Of the weaker lines, we may accept that at 1100 cm^{-1} without question; the 1155 cm^{-1} line is also probably real. Two observers found a line near 300 cm^{-1}, but the discrepancy in the frequencies given is so serious that this line must be regarded as doubtful. We have rejected the lines at 160, 583 and 702 cm^{-1}, since each was found by a single observer only.

We may correlate the Raman and infra-red frequencies as shown in Table I. It is seen that each Raman frequency is also observed in the infra-red, in agreement with the selection rules (Table III and the following paragraph). The frequency shift is going from liquid to gas is roughly constant, about 20 cm^{-1}. A shift of this magnitude is quite reasonable in the case of a polar liquid such as methyl ether.

[3] W. W. Coblentz, *Investigations of Infrared Spectra* (Carnegie Institute of Washington, 1905), Part I.
[4] R. Ananthakrishnan, Proc. Ind. Acad. Sci. **A5**, 285 (1937).
[5] M. Vol'kenstein and Ya. K. Syrkin, Nature **139**, 288 (1937).
[6] S. C. Sirkar, Ind. J. Phys. **7**, 257 (1932).
[7] A. Dadieu and K. W. F. Kohlrausch, Monats. f. Chemie **57**, 225 (1931).
[8] K. W. F. Kohlrausch, Monats. f. Chemie **68**, 349 (1936).

Assignments

Although we shall not attempt a quantitative vibrational analysis at present, certain qualitative conclusions may be pointed out. The highest symmetry which the methyl ether molecule may have corresponds to the group C_{2v}; on this basis the normal coordinate representation, including two internal rotations, would have the structure $\Gamma = 7A_1 + 4A_2 + 4B_1 + 6B_2$. The various "group frequencies" which may be expected are apportioned among the symmetry classes as shown in Table III. The selection rules, which are not particularly helpful, are also given in this table.

TABLE I. *The vibrational spectra of methyl ether.*

INFRA-RED		RAMAN*	
FREQUENCY cm^{-1}	INTENSITY**	FREQUENCY cm^{-1}	INTENSITY POLARIZATION†
—	—	300	?, *P*
below 440	?	412	1, *P*
610	*w*	—	—
920	*m*	920	5, *P*
940	*s*		
1102	?	1100	0, ?
1122	*m*		
1180	*s*	1155	0, *D*
1466	*vs*	1450	4, *D*
1605	*w*	—	—
1862	*m*	—	—
2033	*m*	—	—
2101	*ms*	—	—
2325	?	—	—
2400	*mw*	—	—
2653	*w*	—	—
		2810	10, *P*
		2863	6, *P*
2915	*vs*	2916	5, *P*
		2951	4, *P*
		2986	6, *P*
4274	*m*	—	—

* See Table II, and text.
** *s* = strong, *m* = medium, *w* = weak, *vs* = very strong.
† *P* = polarized, *D* = depolarized.

TABLE II. *Raman data for methyl ether.**

A†	V AND S	S	D AND K	K
160($\frac{1}{2}$)P	—	—	—	—
300(0)P	—	333(0)	—	—
412(1)P	408	416(0)	—	416(0)
—	—	—	—	(583(0?))
—	—	—	—	(702(00?))
916(b)P	921	921(2)	924(2)	920(5)
1105 ?	1095	1102(0)	—	1095($\frac{1}{2}$)
1155($\frac{1}{2}$)D	—	—	(1150(1))	—
1445(6)D	1448(2)	1454(1)	1451(1)	1450(3)
2810(10)P	2813(10)	2814(7)	2814(5)	2813(10)
2863(6)P	2868(3)	2869(3)	(2862(2))	2862(6)
2916(5)P	2908(3)	2921(3)	2914(2)	2917(5)
2951(4)P	2947(2)	2952(3)	2953(2)	2949(3)
2986(6)P	2988(6)	2989(3)	2990(2)	2986(6)

* Frequencies in cm^{-1}; relative intensities as given by each author
† A = Ananthakrishnan, reference 4; V and S = Vol'kenstein and Syrkin, reference 5; S = Sirkar, reference 6; D and K = Dadieu and Kohlrausch, reference 7; K = Kohlrausch, reference 8.

The frequencies of the ν_H and $\delta_{H,\perp}$ types are well known and quite constant in different molecules. The $\delta_{H,\parallel}$ frequency is more variable, ranging from 1250 to 1480 cm^{-1} in the methyl halides; in methyl ether we should expect it to lie somewhat below 1450 cm^{-1}, due to $\delta_{H,\perp} - \delta_{H,\parallel}$ interactions in the A_1 and B_2 classes. The estimate of 1100–1200 cm^{-1} for the CH_3 rocking frequency τ_M is derived from comparison with the methyl halide frequencies. The C–O frequencies $\nu_M(\pi)$ and $\nu_M(\sigma)$ should lie near the 1030 cm^{-1} frequency of methyl alcohol; the third "water-type" frequency, δ_M, is more uncertain.

With these considerations in mind, the tentative assignment of fundamental frequencies shown in Table IV seems most probable. Gas-phase (infra-red) frequencies have been used in this table, except for the 412-cm^{-1} Raman frequency, which lies too low to be observed in the infra-red. The assignments of $\nu_M(\sigma)$, $\nu_M(\pi)$ and δ_M agree with those given by Kohlrausch[8] and by Bonner.[9]

TABLE IV. *Tentative assignments for fundamental frequencies of methyl ether.*

TYPE	NUMBER OF VIBRATIONS	FREQUENCY
ν_H	6	2900
$\delta_{H,\perp}$	4	1466
$\delta_{H,\parallel}$	2	1466?
τ_M	4	1180
$\nu_M(\sigma)$	1	1122
$\nu_M(\pi)$	1	940
δ_M	1	(412)*
γ	2	?

* Liquid-phase frequency.

The considerations summarized in Table III would lead one to expect at least two frequencies near 1450 cm^{-1}, since the $\delta_{H,\perp}$ and $\delta_{H,\parallel}$ vibrations fall in the same symmetry classes in two cases (A_1 and B_2), and should split apart by classical resonance even if they would otherwise fall together. The infra-red spectrum shows quite clearly, however, a single sharp band in this region (1466 cm^{-1}). The assignment of the $\delta_{H,\parallel}$ frequency is accordingly rather puzzling. The possibility of this frequency being too weak to be detected must of course be taken into account.

[9] L. G. Bonner, J. Chem. Phys. **5**, 293 (1937).

TABLE III. *Types of vibration in methyl ether.*

DESIGNATION*	SYMMETRY** $A_1(\pi, s)$	$A_2(\sigma, a)$	$B_1(\pi, a)$	$B_2(\sigma, s)$	TOTAL NUMBER	TYPE	APPROXIMATE FREQUENCY TO BE EXPECTED cm^{-1}
γ	0	1	1	0	2	"Internal rotation"	?
ν_H	2	1	1	2	6	C–H stretching	2900
$\delta_{H,\perp}$	1	1	1	1	4	C–H bending	1450
$\delta_{H,\parallel}$	1	0	0	1	2	C–H bending	~1400
τ_M	1	1	1	1	4	CH_3 rocking	~1100–1200
ν_M	1	0	0	1	2	C–O stretching	~1000
δ_M	1	0	0	0	1	C–O–C deformation	low
Totals	7	4	4	6	21		
Raman-active†	+	+	+	+			
Infra-red-active†	+	−	+	+			

* $\parallel, \perp$ = parallel and perpendicular, respectively, to the C–O axis of the methyl group involved.
** π, σ = symmetric and antisymmetric, respectively, to plane bisecting the C–O–C angle. s, a = symmetric and antisymmetric, respectively, to plane of the C and O atoms.
† +, − = active and inactive, respectively.

The five Raman lines near 2900 cm^{-1} are undoubtedly to be assigned to the ν_H frequencies, together with the overtones of the δ_H frequencies, which will resonate with the 2900 cm^{-1} fundamentals. The single infra-red band found at 2915 cm^{-1} is probably an unresolved complex of several frequencies; the resolution of our instrument is quite low in this region.

With regard to the frequency of the torsional oscillations, γ, there is the interesting possibility that the Raman line at 300 cm^{-1}, if real, corresponds to this motion. Reliable information on this point, however, must await the complete vibrational analysis and accurate thermal data.

In concluding, we should like to express to Professor E. B. Wilson, Jr., our appreciation of the use of his laboratory, and of many helpful discussions during this work.

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The Prediction of Rate Constants from Equilibrium Data for Reactions in D_2O-H_2O Mixtures

FRANK BRESCIA
College of the City of New York, New York, New York

(Received February 15, 1939)

The concentrations of hydrogen and deuterium ions at different fractions of D in the solvent are calculated from the simultaneous solution of the equations $C_{H^+}\cdot C_{HDO}/C_{D^+}\cdot C_{H_2O}=3.76$ and $C_{H^+}+C_{D^+}=$concentration of strong acid. Similarly, the concentrations of hydroxyl and deuteroxyl ions are calculated from the equations $C_{OD^-}\cdot C_{H_2O}/C_{OH^-}\cdot C_{HDO}=0.225$ and $C_{OH^-}+C_{OD^-}=$concentration of alkali. It is then possible to predict reaction rates for specific hydrogen ion and specific hydroxyl ion catalyzed reactions, in mixtures of H_2O-D_2O, on the assumption that the rate is proportional to the fraction of D^+ in the first case and to the fraction of OD^- in the second.

IT IS possible to predict the rate constant for specific hydrogen ion and hydroxyl ion catalyzed reactions in mixtures of deuterium and protium oxides from equilibrium data.

From the equilibrium equation[1]

$$K_1=\frac{C_{H^+}\cdot C_{HDO}}{C_{D^+}\cdot C_{H_2O}}=3.76 \qquad (1)$$

and from the equation

$$C_{D^+}+C_{H^+}=\text{Concentration of Strong Acid} \qquad (2)$$

TABLE I. *Concentration of* H^+, D^+, OH^- *and* OD^- *at different fractions of* D *in the solvent.*

F_D*	C_{H^+}	C_{D^+}	C_{OH^-}	C_{OD^-}
0.00	1.00	0.00	1.00	0.00
26.40	0.848	0.152	0.868	0.132
55.60	.627	.373	.665	.335
78.49	.376	.624	.417	.583
92.51	.152	.848	.175	.825
100.00	.00	1.00	.00	1.00

* $F_D=\Delta S(100)/0.1079=$Fraction of deuterium in the solvent.

[1] F. Brescia, J. Am. Chem. Soc. **60**, 2811 (1938).

in any D_2O-H_2O mixture, the value of C_{H^+} and C_{D^+} can be calculated for different fractions of D in the solvent. The water concentrations, C_{HDO} and C_{H_2O}, are calculated from the equilibrium process[2] $H_2O+D_2O=2HDO$ for which $K=3.27$. A summary of the C_{H^+} and C_{D^+} values when the concentration of HCl is one molar is given in Table I.

The rate constant, k, at different fractions of D may then be calculated from these values of C_{H^+} and C_{D^+}, and from the values of the specific rate constant in ordinary water, k_{H^+}, and in $F_D=100$ solvent, k_{D^+}, on the simple assumption that

$$k=k_{H^+}C_{H^+}+k_{D^+}C_{D^+}. \qquad (3)$$

This procedure was carried out for the reactions: the hydrolysis of acetal,[3] the hydrolysis of methyl acetate,[4] and the hydrolysis of ethyl

[2] B. Topley and H. Eyring, J. Chem. Phys. **2**, 217 (1934).
[3] W. J. C. Orr and J. A. V. Butler, J. Chem. Soc. (London) **1937**, 330.
[4] W. E. Nelson and J. A. V. Butler, J. Chem. Soc. (London) **1938**, 957.

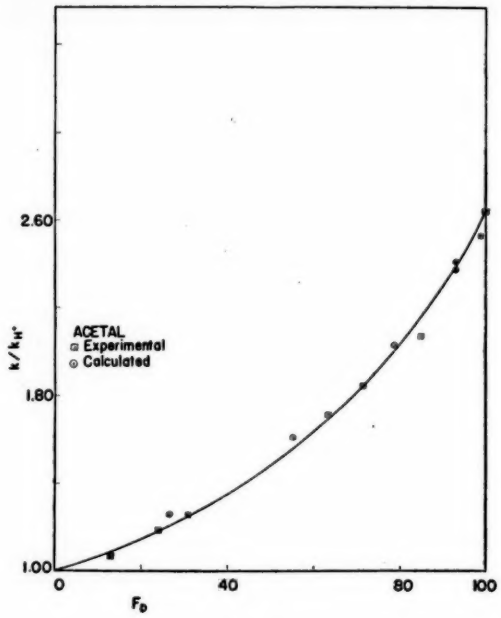

FIG. 1.

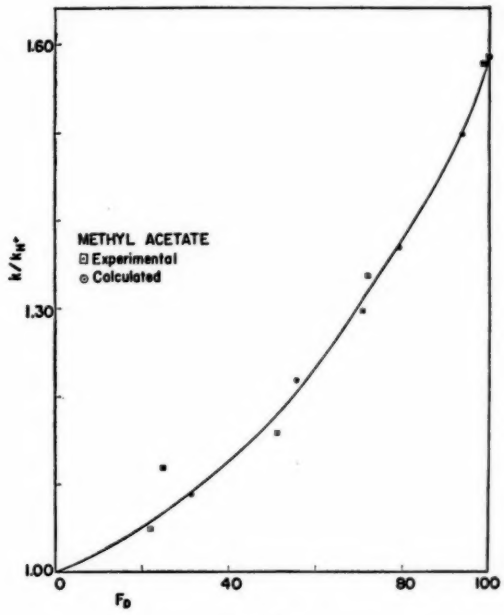

FIG. 2.

formate[4] which have been experimentally studied over a range of deuterium solvents. The values of k_{D^+} for the hydrolysis of ethyl formate and of methyl acetate reactions were extrapolated from the experimental data. In all other cases, the original author's extrapolated value for k_{D^+} was

TABLE II. *Summary of calculated and experimental values of* k/k_{H^+}.

	ACETAL		METHYL ACETATE		ETHYL FORMATE		
F_D	EXP.[3]	CALC.	EXP.[4]	CALC.	EXP.[4]	CALC.	CALC.
0.00	1.00	(1.00)	1.00	(1.00)	1.00	(1.00)	(1.00)
12.4	1.074						
21.4			1.05				
24.1	1.19						
26.40		1.25		1.09		1.07	1.06
26.5			1.12				
27					1.04		
30.9	1.25						
51.2			1.16				
55.60		1.61		1.22		1.16	1.14
63.3	1.715						
70.3			1.30				
71.3	1.85		1.34				
72					1.20		
78.49		2.03		1.37		1.27	1.23
82					1.27		
84.8	2.08						
92.51		2.39		1.50		1.36	1.31
96					1.39		
98.4			1.58				
98.5	2.51?						
100.0	(2.64)	(2.64)	(1.59)	(1.59)	(1.43)	(1.43)	(1.37)

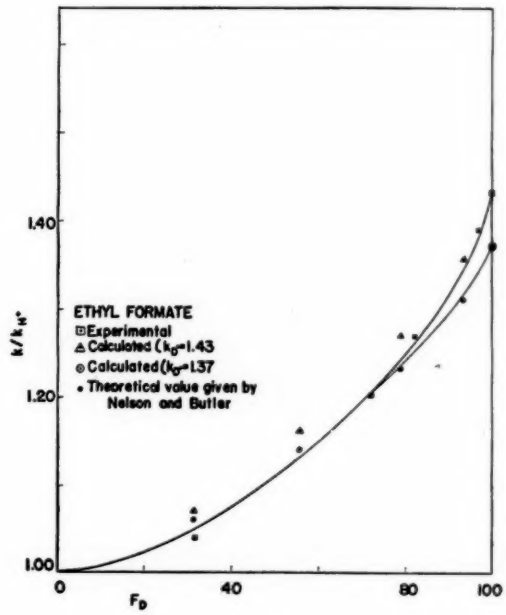

FIG. 3.

used. The experimental data and calculated values are summarized in Table II and plotted in Figs. 1, 2 and 3. In each case, the agreement between the calculated and the measured rate is within the experimental error. It should be noted in the case of ethyl formate that "considerable difficulty was experienced in obtaining stable

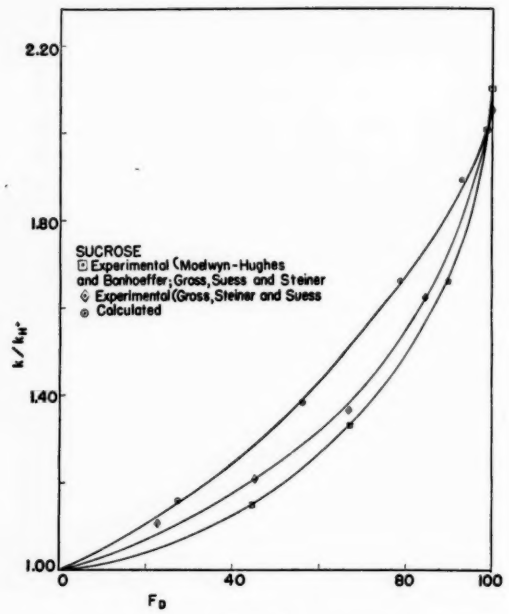

FIG. 4.

final readings and the accuracy of the series is not great."[4] If the theoretical value (1.37), given by Nelson and Butler,[4] for the k_{D^+} for the ethyl formate reaction is used, better agreement is obtained.

The same procedure applied to the sucrose inversion in H_2O-D_2O mixtures does not yield results in agreement with the available experimental data[5] which, in itself, is not consistent. In the mutarotation of glucose reaction, which is exceptional in that the k_{D^+} is smaller than the k_{H^+}, the theoretical curve shows a positive deviation from linearity whereas the best curve through the experimental data[6] is a straight line. The calculated and experimental results for these reactions are given in Table III and plotted in Figs. 4 and 5.

This method is analogous in principle to that employed by Hamill and La Mer[7] except that they used the equilibrium equation

$$\frac{C_{D_2O}\cdot C^2_{H^+}}{C_{H_2O}\cdot C^2_{D^+}}=15.7 \qquad (4)$$

calculated by Korman and La Mer[8] from electromotive force data whereas the equation

$$\frac{C_{H^+}\cdot C_{HDO}}{C_{D^+}\cdot C_{H_2O}}=3.76 \qquad (1)$$

has been independently calculated from kinetic measurements.

The derivation of a value for the equilibrium constant for the process

$$OH^-+HDO=H_2O+OD^- \qquad (5)$$

permits the similar calculation of the rate constant for a specific hydroxyl ion catalyzed reaction in mixtures of D and H waters. This is now accomplished as follows. The equilibrium constants of the following processes are known:[1, 2, 9]

$$D_2O=D^++OD^-;\quad K_{DW}=\frac{1.95\times10^{-15}}{55.15}, \qquad (6)$$

$$H_2O=H^++OH^-;\quad K_{HW}=\frac{10^{-14}}{55.33}, \qquad (7)$$

$$D^++H_2O=H^++HDO;\quad K_8=3.76, \qquad (8)$$

$$D_2O+H_2O=2HDO;\quad K_9=3.27. \qquad (9)$$

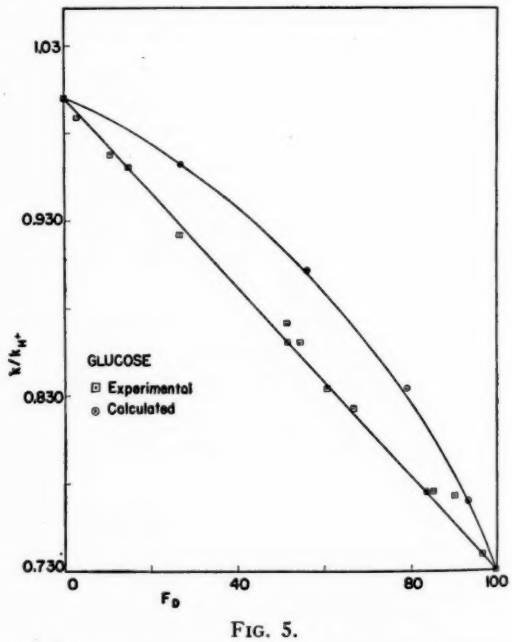

FIG. 5.

[5] (a) E. A. Moelwyn-Hughes and K. F. Bonhoeffer, Naturwiss. **22**, 174 (1934); P. Gross, H. Suess and H. Steiner, *ibid.* **22**, 662 (1934); (b) P. Gross, H. Steiner and H. Suess, Trans. Faraday Soc. **32**, 883 (1936).

[6] W. H. Hamill and V. K. La Mer, J. Chem. Phys. **4**, 395 (1936).

[7] W. H. Hamill and V. K. La Mer, J. Chem. Phys. **4**, 294 (1936).

[8] S. Korman and V. K. La Mer, J. Am. Chem. Soc. **58**, 1396 (1936).

[9] W. F. K. Wynne-Jones, Trans. Faraday Soc. **32**, 1397 (1936).

Subtracting (7) from (6) and adding (8) yields

$$D_2O+OH^-=HDO+OD^-;\ K_{10}=0.736. \quad (10)$$

Subtracting (9) from (10) yields

$$OH^-+HDO=H_2O+OD^-;\ K_{11}=0.225. \quad (11)$$

Doubling (10) and subtracting (9) yields

$$D_2O+2OH^-=H_2O+2OD^-;\ K_{12}=0.166. \quad (12)$$

The value for K_{12} is much lower than the value, 0.413, calculated by Korman and La Mer[8] from electromotive force measurements.

From the value of the equilibrium Eq. (11) and from the equation

$$C_{OH^-}+C_{OD^-}=\text{Concentration of Alkali} \quad (13)$$

in any D_2O-H_2O mixture, the values of C_{OD^-} and C_{OH^-} can be calculated at different fractions of D in the solvent. A summary of these values when the concentration of alkali is one molar is given in Table I.

On the analogous assumption that

$$k=k_{OH^-}C_{OH^-}+k_{OD^-}C_{OD^-}, \quad (14)$$

where k_{OH^-} and k_{OD^-} are the specific rate constants in $F_D=0$ and $F_D=100$ solvent, the rate constant, k, at different fractions of D may be calculated. This was done for the decomposition of diacetone alcohol[4] and the results (Table III) are in very poor agreement with the experimental curve (Fig. 6). On the other hand, if the value of K_{11} is calculated from Korman and La Mer's value for K_{12} and from K_9, it is found to be 0.355 instead of 0.225. Repetition of the calculation of k based on the value 0.355 for K_{11} yields results (Table III, Fig. 6) very close to the experimental data. A slight but definite sag in the curve is observed whereas the available data indicates a straight line relation between k and F_D.

TABLE III. *Summary of calculated and experimental values of k/k_{H^+} and k/k_{OH^-}.*

F_D	Sucrose, k/k_{H^+}			Glucose, k/k_{H^+}		Diacetone Alcohol, k/k_{OH^-}		
	Exp.[5a]	Exp.[5b]	Calc.	Exp.[6]	Calc.	Exp.[4]	Calc.*	Calc.†
0.00	1.00	1.00	(1.00)	1.00	(1.00)	1.00	(1.00)	(1.00)
3.5				0.987				
10.8				.965				
12.1						1.06		
14.5				.958				
22.5		1.11						
25.9						1.12		
26.40			1.16		0.959		1.06	1.09
26.5				.920				
44.4	1.15							
44.7		1.21						
50.7				.871				
51.				.859				
52.9						1.22		
54.				.859				
55.60			1.39		.899		1.15	1.20
60.				.833				
66.3				.823				
66.6		1.37						
67.1	1.33							
72.5						1.33		
78.49			1.66		.832		1.26	1.31
83.1				.775				
84.				.775				
84.2		1.63						
85.3						1.39		
89.				.772				
90.	1.66							
92.51			1.89		.771		1.38	1.40
96.				.740				
98.1	2.01							
98.4		2.01						
99.						1.44		
99.6						1.45		
100.0	(2.10)	(2.05)	(2.05)	(0.730)	(0.730)	(1.45)	(1.45)	(1.45)

* Calculations based on $K_{11}=0.225$.
† Calculations based on $K_{11}=0.355$.

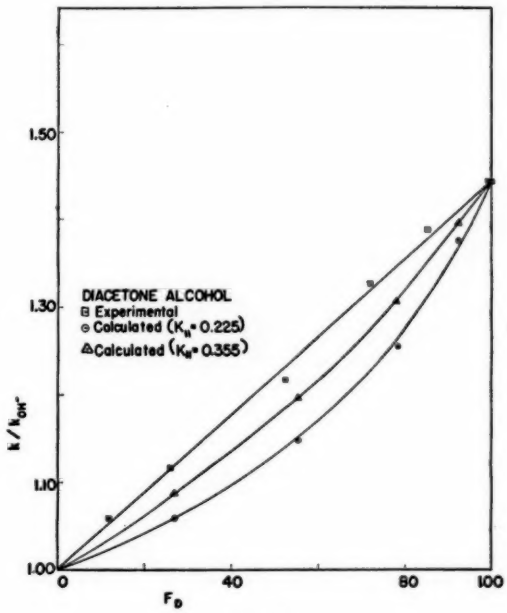

FIG. 6.

The predicted rates are in good agreement, on the whole, with the available experimental rates for specific hydrogen ion catalyzed reactions in which the rate is faster in D_2O. It is difficult to draw conclusions for the base catalyzed reaction since only one set of experimental data is available for comparison. It is quite possible that the lack of agreement in the sucrose, glucose and diacetone alcohol reactions may be due to substrate exchange with solvent. Preliminary results[10] seems to indicate the possibility that the rate of the base catalyzed reaction of nitramide decomposition is a linear function of F_D. Nitramide also exchanges with the solvent.

[10] S. Hochberg and V. K. La Mer, unpublished.

The Transference Numbers of Sodium Acetate in Aqueous Solution

D. J. LeRoy and A. R. Gordon
Chemistry Department, University of Toronto, Toronto, Canada
(Received March 3, 1939)

The transference numbers for sodium acetate in aqueous solution at 25°C for the concentration range $0.02N$–$0.17N$ have been determined by the same method as was used for potassium acetate. The results are in close but not exact agreement with those previously reported by Longsworth. The Longsworth function $t_+^{0'}$ is linear in the concentration only up to $0.1N$.

IN a previous paper,[1] we reported the transference numbers for potassium acetate in aqueous solution; although this work on the acetates has been discontinued, it still seems desirable to report our results for sodium acetate, especially as our values are in close but not exact agreement with those of Longsworth.[2]

The apparatus, the preparation of the solutions, and the general technique of the measurements were the same as for potassium acetate;[1] both cell I (descending boundary with lithium acetate indicator) and cell II (ascending autogenic boundary with cadmium acetate indicator) were employed; in the majority of the measurements, current-time readings were used to determine the number of coulombs required to displace the boundary through a known volume, in the remainder, microcoulometers. Table I summarizes the results; the first column shows the cell used, the second gives the concentration C in equivalents per liter, the third the mean value of $t_{+\,\mathrm{obs}}$ obtained from (in general) two or more independent runs, the fourth and fifth the volume and solvent corrections,[3] and the last the value of $t_{+\,\mathrm{corrected}}$.

TABLE I. *Sodium acetate, 25°C.*

Cell	C	$t_{+\mathrm{obs}}$	Sol. Corr.	Vol. Corr.	$t_{+\mathrm{corr}}$
II	0.02190_4	0.5557	0.0005	−0.0002	0.5560
II	0.04140_8	0.5572	0.0003	−0.0004	0.5571
I	0.05117_1	0.5584	0.0002	−0.0008	0.5578
II	0.06956	0.5596	0.0002	−0.0007	0.5591
I	0.10074	0.5618	0.0001	−0.0016	0.5603
II	0.10155	0.5609	0.0001	−0.0010	0.5600
II	0.15788	0.5625	0.0000	−0.0016	0.5609
I	0.16044	0.5631	0.0000	−0.0026	0.5605

[1] D. J. LeRoy and A. R. Gordon, J. Chem. Phys. **6**, 398 (1938).
[2] L. G. Longsworth, J. Am. Chem. Soc. **57**, 1185 (1935).
[3] For the method of computing these corrections, and for the data used, see references 1 and 2.

Longsworth[4] has shown that for many 1–1 electrolytes in dilute solution, a plot of his function $t_+^{0'}=(t_+\cdot\Lambda'+\beta\sqrt{C})/(\Lambda'+2\beta\sqrt{C})$ where $\Lambda'=\Lambda_0-(\alpha\Lambda_0+2\beta)\sqrt{C}$, Λ_0 is the equivalent conductance at infinite dilution, and α and β are theoretical constants whose values for 1–1 electrolytes in aqueous solution at 25°C are 0.2274 and 29.90, is linear in C. Fig. 1 shows a plot of $t_+^{0'}$ computed not only from our data but from those of Longsworth as well; it is evident that our results are on the average about 0.0004 greater than his, a difference that is somewhat larger than the apparent error of the measurements. It is also evident that while $t_+^{0'}$ is linear in C up to $C=0.1$, it deviates definitely from

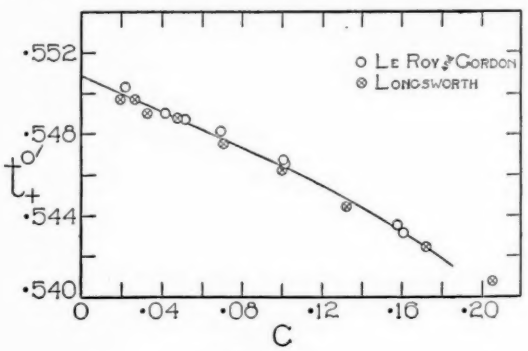

FIG. 1.

linearity for higher concentrations, in distinction from potassium acetate for which $t_+^{0'}$ is linear up to $C=0.16$. If the "best" curve (as shown) be drawn through both sets of data, $t_+^{0'}$ for $C<0.1$, is given by the equation $t_+^{0'}=0.5509-0.045C$.

MacInnes and Shedlovsky[5] give 90.97 as the limiting equivalent conductivity of sodium acetate at 25°; this value is subject to correction

[4] L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).
[5] D. A. MacInnes and T. Shedlovsky, J. Am. Chem. Soc. **54**, 1429 (1932).

owing to the calibration on which it is based, but for computing transference numbers at infinite dilution it is justifiable to use it provided the corresponding limiting ionic mobility for sodium ion (50.10) is employed. It was previously shown,[1] however, that MacInnes and Shedlovsky's data could be represented more closely by the equation $\Lambda_0' = 90.94 + 101._1 C$ than by the equation they employ $\Lambda_0' = 90.97 + 90C$; here Λ_0' is the Onsager function $(\Lambda + 2\beta\sqrt{C})/(1 - \alpha\sqrt{C})$ where Λ is the equivalent conductivity at concentration C. Even better agreement with the experimental data is obtained if the extended Onsager-Shedlovsky equation[6] is employed

$$\Lambda_0' = 90.94 + 152._1 C + 20._7 C \log C. \qquad (1)$$

[6] L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932); T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. **56**, 1066 (1934); T. Shedlovsky, A. S. Brown and D. A. MacInnes, Trans. Electrochem. Soc. **66**, 165 (1934); A. R. Gordon, J. Chem. Phys. **7**, April (1939). If δ indicates the difference $\Lambda_{calc} - \Lambda_{obs}$, the closer agreement of Eq. (1) above with the experimental data, as compared with MacInnes and Shedlovsky's Eq. (5) is evident from the following table. The comparison is for the fourteen solutions listed in their Table I.

	$\Sigma\delta^2$	$\Sigma\delta$	$\Sigma\|\delta\|$	Max.$\|\delta\|$
MacInnes and Shedlovsky, Eq. (5)	2.88	0.14	0.48	0.11
This paper, Eq. (1)	1.90	0.00	0.38	0.07

TABLE II.

C	0	0.01	0.02	0.05	0.10	0.15
t_+	0.5509	0.5540	0.5553	0.5575	0.5598	0.5606

In any event, the conductance data correspond more nearly to $\Lambda_0 = 90.94$ than to $\Lambda_0 = 90.97$, i.e., t_+^0 for sodium acetate should be 0.5509, in exact agreement with the result obtained from the mean plot of Fig. 1. Table II gives values of t_+ for a few round values of the concentration; the entries are on the average about 0.0003 greater than those given by Longsworth[2] in his Table VI; this is within his estimated probable error for that table.

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The Thermal Decomposition of Methylene Diacetate, Ethylidene Diacetate and Paracetaldehyde at Low Pressures

J. R. DACEY AND C. C. COFFIN
Physical Chemistry Laboratory, Dalhousie University, Halifax, Canada

(Received February 16, 1939)

By means of an optical lever manometer the decomposition velocities of methylene diacetate, ethylidene diacetate and paracetaldehyde have been measured down to pressures of 0.05 mm. of mercury. No falling off in reaction rate has been observed. The minimum numbers of internal degrees of freedom contributing to the activation energies are thus 16, 18 and 64, respectively.

INTRODUCTION

IT has been shown[1] that ethylidene diacetate, paracetaldehyde and their homologs decompose in the vapor state by a homogeneous first-order mechanism. The apparatus employed did not permit satisfactory rate measurements to be made at initial pressures lower than several centimeters of mercury. The present paper deals with measurements at initial pressures between 0.05 and 3 millimeters.

[1] C. C. Coffin *et al.*, Can. J. Research **5**, 636 (1931); **6**, 417 (1932); **7**, 75 (1932); **9**, 603 (1933); **11**, 180 (1934); **15**, 229 (1937); **15**, 247 (1937); **15**, 254 (1937); **15**, 260 (1937). Trans. Roy. Soc. Can. **27**, 161 (1933).

EXPERIMENTAL

The pressure change at constant volume was followed with an optical lever manometer resembling that of Shrader and Ryder,[2] mounted in a heavy iron frame resting on large rubber stoppers on the concrete basement floor. A small glass bulb attached to a lever arm and mirror and carried by a fine torsion wire floated on the mercury in one arm of the manometer. The torsion wire was stretched across the prongs of a spring brass fork inserted and adjusted from

[2] J. E. Shrader and H. M. Ryder, Phys. Rev. **13**, 321 (1919).

TABLE I. *Summary of reaction velocity data.*

RUN NO.	INITIAL P	$T°$ ABS.	$k \times 10^4$	$-\log k$	$1/T \times 10^3$
		Methylene Diacetate			
25	0.90 mm	590.6	16.8		
26	.36	589.2	22.5		
27	.14	589.2	21.9	2.665	1.696
28	.20	589.2	20.6		
29	.40	589.3	26.0		
1	.29	585.1	18.5		
2	.26	585.1	20.1		
3	.22	585.2	19.4		
4	.23	585.1	21.0	2.708	1.709
5	.37	585.0	18.5		
6	.34	585.0	20.4		
7	.32	577.0	11.7		
8	.22	577.0	11.7		
9	.30	577.0	13.2	2.932	1.733
10	.39	577.1	9.3		
11	.26	577.2	12.4		
12	.32	569.8	8.29		
13	.52	569.7	7.39		
14	.41	569.4	7.15		
15	.14	569.7	7.53	3.137	1.755
16	.36	569.8	6.96		
17	.39	569.7	6.45		
18	.35	552.6	2.15		
19	.38	551.9	2.82		
20	.30	552.2	2.96		
21	.35	552.6	3.15	3.516	1.810
22	.26	552.7	3.45		
23	.36	552.6	3.36		
24	.33	552.6	3.45		
		Ethylidene Diacetate			
1	.49 mm	570.1	6.97		
2	.60	570.1	7.68		
3	.40	570.1	7.30	2.121	1.755
4	.40	570.1	8.20		
5	.74	566.5	7.65		
6	.52	558.6	3.00		
7	.35	558.6	3.40	2.495	1.790
8	.37	551.6	2.78		
9	.60	554.8	2.83		
10	.57	554.8	3.37	2.551	1.807
11	.52	550.3	2.35		
12	.36	552.7	2.74		
13	.22	537.1	1.60		
14	.25	537.1	1.60		
15	.80	538.4	1.00		
16	.44	538.4	1.09	2.910	1.858
17	.68	538.4	1.00		
18	.62	538.4	1.22		
19	.30	538.4	1.11		
20	.18	531.1	7.42		
21	.59	532.6	7.61		
22	.34	533.5	10.09		
23	.46	530.2	11.50		
24	.50	534.4	7.61	3.015	1.881
25	.42	530.2	12.80		
26	.35	530.1	10.70		
27	.40	530.1	11.30		
28	.55	533.6	7.91		
29	0.72 mm	519.8	2.02		
30	.43	519.8	3.15		
31	.66	519.8	2.82		
32	.73	519.9	2.82	3.556	1.923
33	.55	519.9	2.83		
34	.58	519.0	2.54		
35	.52	520.0	3.32		
36	.29	509.1	2.86		
37	.34	509.3	2.03	3.634	1.962
38	.42	509.4	2.42		
39	.34	509.6	1.97		
		Paracetaldehyde			
1	.90 mm	566.4	112		
2	1.19	566.3	112		
3	1.99	566.0	109	1.932	1.765
4	1.03	566.7	118		
25	.27	566.1	120		
26	.27	567.2	129		
27	.20	583.4	402		
28	1.10	584.2	403		
29	.40	583.6	404	1.388	1.713
30	.20	585.4	428		
31	.27	583.6	406		
32	.05	573.1	182		
33	.39	573.2	179		
34	.40	574.2	188		
35	.22	574.0	178		
36	.23	573.8	188		
37	.15	574.4	199	1.735	1.742
38	.14	572.9	177		
39	.11	575.2	177		
40	.10	572.8	183		
41	.25	574.0	176		
42	.25	574.0	168		
43	.90	573.2	161		
5	.79	554.7	48.0		
6	1.76	554.7	52.6		
7	1.17	556.6	54.9		
8	1.21	553.8	48.3	2.296	1.80?
9	1.16	554.0	49.6		
10	3.28	554.7	52.0		
11	.99	554.7	49.0		
12	.74	544.3	21.0		
13	.67	544.2	21.8	2.674	1.838
14	.88	543.6	20.9		
15	.50	541.8	20.0		
16	.55	540.1	18.6	2.740	1.851
17	.99	538.4	15.0		
18	1.65	524.2	5.68		
19	1.50	524.2	5.55		
20	.80	525.1	5.53		
21	1.05	525.7	5.41	3.263	1.904
22	1.03	524.3	4.99		
23	.87	524.8	5.18		
24	.85	525.9	5.91		

above through a ground glass and Picein joint. The two sides of the manometer, a short U-tube of 6-cm Pyrex, were connected by a stopcock. The spot of light from the mirror was brought through the wall of the manometer tube and focused on a vertical ground glass scale. Three different combinations of lenses, floats and lever arms were used magnifying the mercury movement 50, 91 and 250 times. Actual pressures were obtained by frequent calibration over the whole range against an oil manometer.

The reaction chamber was an 11. Pyrex flask sealed inside a 21. flask in such a way that it could be heated by the vapor of mercury boiling under a definite pressure. It was connected by stopcocks with pumps and reactant reservoir. To smooth out vibrations from the bumping mercury in the boiler the manometer and reaction chamber were connected through a 5-turn 8-cm spiral of very thin-walled 4-mm tubing. The dead space due to the manometer and connecting tubing was less than 3 percent of the total volume and is not taken into account in the following calculations.

Several different samples of each reactant were studied. They were purified as already described.[1]

Results

The results obtained are summarized in Table I. In all cases readings were taken at equal time intervals and velocity constants calculated by the method of Guggenheim.[3]

In Fig. 1, $-\log k$ is plotted against $1/T$. The straight lines of the figure are those given by the previously published rate equations.[1] It is evident that no falling off in rate occurs in this pressure range. The fact that the methylene diacetate points are appreciably above the line is probably due to the increased importance of the heterogeneous reaction[4] at the lower pressures. A steady drift in the final pressure always occurred in the runs with this ester.

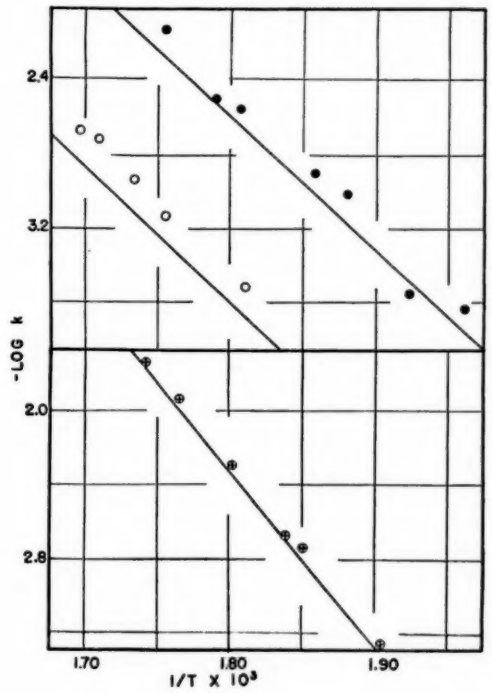

FIG. 1. Reaction rates at low pressures. ●, methylene diacetate; ○, ethylidene diacetate; ⊕, paracetaldehyde.

Following the treatment of Hinshelwood[5] the minimum number of contributing squared terms is found to be about 16, 18 and 64 for methylene diacetate, ethylidene diacetate and paraldehyde, respectively. Molecular diameters are taken as 4×10^{-8} cm.

Since this work was done Burnett and Bell have published data on paraldehyde that checks with the above results.[6]

A Bursary from the National Research Council of Canada is acknowledged by one of us (J. R. D.).

[3] E. A. Guggenheim, Phil. Mag. **2**, 543 (1926).
[4] C. C. Coffin and W. B. Beazley, Can. J. Research **15**, 233 (1937).
[5] C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, 1933).
[6] R. le G. Burnett and R. P. Bell, Trans. Faraday Soc. **34**, 420 (1938).

The Solid State of H_2, HD and D_2

MARCUS E. HOBBS
Department of Chemistry, Duke University, Durham, North Carolina
(Received February 20, 1939)

By using the van der Waals field as calculated for H_2 from the second virial coefficient by Lennard-Jones, and the kinetic zero point energy expression given by London in the theory of liquid He, the lattice energies of solid H_2, HD and D_2 have been calculated. The values calculated for the energy at 0°K are for H_2 −180.4 and for D_2 −280.6 calories per mole. These are in good agreement with the experimental values of −183.4 and −274.0 cal./mole, respectively. The corresponding theoretical values of the volume are 23.24 cc (22.65 obs.) for H_2, and 19.78 cc (19.56 obs.) for D_2. The values of HD have been predicted.

INTRODUCTION

THE energy and volume of liquid and solid He have been accounted for by London[1] (hereafter L.) who showed that the kinetic zero point energy has a marked effect on these properties. In fact, it was found that the zero point motion prevents He from solidifying except under pressure (25 atmos. at 0°K). In the case of H_2 the smaller mass leads one to expect similar effects, so it may be of interest to show why H_2, in spite of its smaller mass, solidifies under its own vapor pressure. It might be expected that this difference could be accounted for by the fact that the van der Waals attractive forces of H_2 are much larger than those of He (about 10 times). We shall show, in fact, that the attractive forces of H_2 are strong enough to establish a lattice of the close packed type; whereas for He it has been shown that this structure is realized only under external pressure.

In what follows the expression used for the zero point energy is the same as that used for He, namely

$$E_0=\frac{h^2d}{2\pi m(R-0.891d)^2(R+0.713d)}. \quad (1)$$

Here R is the mean distance between molecules (NR^3=molar volume), m is the mass of each particle, and d is a very roughly idealized diameter. We shall treat d as the adjustable parameter in the following calculations. Expression (1) is an arbitrary interpolation between a formula found by Heitler[2] and Lenz[3]

$$E_0=h^2d/2\pi mR^3, \quad R\gg d$$

which is valid for very low density and the formula

$$E_0=h^2/8m(r-d)^2, \quad r\geq d,$$

which gives an estimate for the case of very high density. In the last equation r is the closest distance in close packing ($r=2^{1/6}R$). The movement of the center of m is confined to the interior of a sphere of radius $(r-d)$.

For the potential energy of each of the three cases, H_2, D_2 and HD, we shall use the same expression, namely

$$\phi=(51/r^9-1.78/r^6)10^{-11} \text{ erg} \quad (2)$$

where ϕ is the potential energy between two molecules, and r is the distance in A. This function is one of three obtained by Lennard-Jones[4] who determined the energy functions so as to give the best representation of the experimental values of the second virial coefficients of H_2.

If ϕ is summed over all molecules for three different regular lattices, the following expressions are obtained for the potential energy per mole:

Face-centered cubic

$$E_{\text{pot}}=(162R^{-9}-9.27R^{-6})10^5 \text{ cal./mole}. \quad (3)$$

[1] F. London, Proc. Roy. Soc. (London) **A153**, 576 (1936). (See also, J. Phys. Chem. **43**, 49 (1939).)

[2] W. Heitler, Zeits. f. Physik **44**, 161 (1927).

[3] W. Lenz, Zeits. f. Physik **56**, 778 (1929); Ann. d. Physik **33**, 630 (1938).

[4] J. E. Lennard-Jones, Proc. Phys. Soc. (London) **43**, 461 (1931).

Simple cubic

$$E_{pot}=(245R^{-9}-10.8R^{-6})10^5 \text{ cal./mole.} \quad (4)$$

Diamond

$$E_{pot}=(556R^{-9}-15.6R^{-6})10^5 \text{ cal./mole.} \quad (5)$$

In these equations R is the mean distance in A between molecules in the particular lattice. The lattice sums used for the face-centered and simple cubic cases were obtained from Lennard-Jones and Ingham's[5] evaluation. The values for the diamond lattice were determined directly by summing over all of the first and second nearest neighbors for the repulsive term, and over all molecules for the attractive term. The result of adding the zero point energy to (3), (4) and (5) is taken as giving the total energy of the system at 0°K. In making this addition we have assumed with L. that the zero point energy is independent of the lattice structure. The same value of d is used for all three molecules. If the respective masses are inserted, the expressions for the zero point energy are

$$E_{0H_2}=\frac{304.0d}{(R-0.891d)^2(R+0.713d)} \text{ cal./mole,} \quad (6)$$

$$E_{0HD}=\frac{202.6d}{(R-0.891d)^2(R+0.713d)} \text{ cal./mole,} \quad (7)$$

$$E_{0D_2}=\frac{152.0d}{(R-0.891d)^2(R+0.713d)} \text{ cal./mole.} \quad (8)$$

For d, the value 2.70A was found to give the best fit. This value seems quite reasonable as it lies between $d_0=3.06$A, the distance of approach for which (2) becomes zero, and $d=2.48$A, the distance of separation for which (2) yields an energy of $+6.60\times10^{-14}$ erg, the equivalent of a temperature of 321°K. The value 2.48A is in close agreement with the diameter given by viscosity which is 2.47A.[6] By comparison the best fitting d value for He is 2.35A which lies between $d_0=2.60$A and $d=1.95$A. The choice of the same value of d for H_2 as for D_2 seems quite justified, but the use of this value for HD is somewhat questionable. The H_2 and D_2 molecules rotate about the midpoint of the line of centers, whereas the HD rotates about a point approximately 0.50A from the H atom and 0.25A from the D atom. If one assumed for the H_2 molecule a diameter 3.06A the HD molecule might be considered as a molecule of diameter approximately $2(0.38-0.25)+3.06=3.32$A. Actually the smallest distance between molecules in the stable close packed structure is found to be 3.77A for H_2 and 3.58A for D_2. Thus, allowing even this maximum diameter of 3.32A, the HD molecule would probably be able to rotate freely without real interference of repulsive fields. In any case, since the distance 0.25 occurs equally as often as 0.50, the value of 0.375 may be as characteristic for HD as for H_2 and D_2. It may be noted that a slight increase of d will cause the zero point energy to increase, thereby effecting a decrease in the negative total energy.

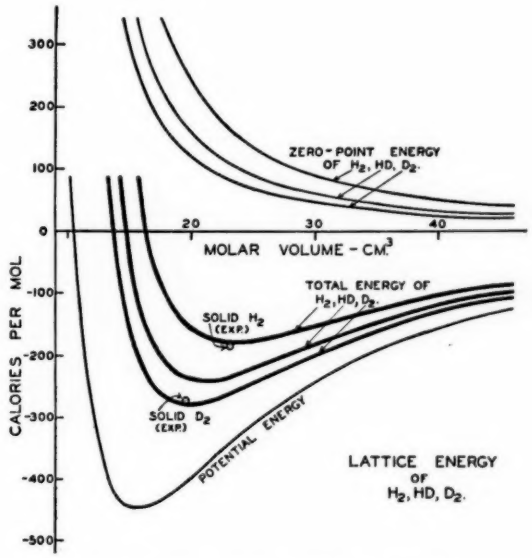

FIG. 1. Energy-volume relations for solid H_2, HD, D_2 at 0°K.

RESULTS AND DISCUSSION

The value of E_0 (with $d=2.70$A) for H_2, HD and D_2 and of E_{pot} for the close-packed structure (Eq. (3)) have been calculated for different values of the molar volume. The results are shown graphically in Fig. 1. The sum of E_0 and E_{pot}, *viz.*, the total energy, is represented in this figure as E, for the respective cases. The experi-

[5] J. E. Lennard-Jones, p. 319, R. Fowler's *Statistical Mechanics*, second edition (University Press, Cambridge, 1936).

[6] H. A. Stuart, *Molekülstruktur*, (Julius Springer, Berlin, 1934). p. 36.

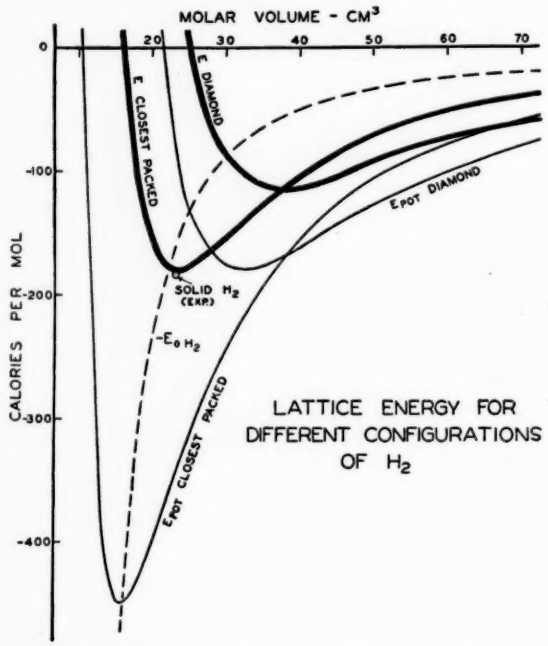

FIG. 2. Lattice energy, E, potential energy, E_{pot}, and the negative of the zero point energy, $-E_0$, for the face-centered cubic, and the diamond lattices of H_2.

mental values of the total energy E, and molar volume, V, for H_2, and D_2 are indicated by the small circles. The zero point energy is seen to be equivalent to an additional repulsive term, the magnitude being such as to have a decisive effect on the observed values of volume and energy. The values of the total energy, E, and volume, V, at the minimum of the E curves in Fig. 1 are given in Table I. In the same table we have also listed the zero point energy, E_0, at the calculated minimum of the total energy. E_{pot} is the potential energy of the close-packed structure at this point, and K is the compressibility.

The observed values of the molar volumes and compressibilities are taken from Simon and Megaw.[7] Their observations were made at 4.2°K and presumably are not very different from those which would be found at 0°K, since the volume change from 4.2°K to 0°K is probably quite small, and is very likely within the experimental errors of the measurements. The observed compressibilities are average values taken over 1 to 100 kg/cm², and therefore claim no particular exactness. The values of the observed heat of sublimation at 0°K were obtained from Clusius and Bartholomé[8] for D_2, and from Simon and Lange[9] for H_2. The Kirchhoff sublimation law was used for the extrapolation to 0°K.*

The values of the zero point energy are of particular interest as they are much smaller than previously calculated values. Scott, Brickwedde, Urey and Wahl[10] calculated values of $E_{0H_2}=318$ cal. and $E_{0D_2}=225$ cal. and indicated that these values are probably too small. Clusius and Bartholomé[8] have calculated $E_{0H_2}=305$ cal. and $E_{0D_2}=215$ cal., and have also indicated that these values are lower limits. Both of the above sets of values have been calculated on the basis of a harmonic zero point vibration, and as such have made the assumption that the zero point energy was inversely proportional to the square root of the mass. In comparison we obtain, using the energy inversely proportional to mass, the values $E_{0H_2}=162$ cal. and $E_{0D_2}=123$ cal. The values of the Debye θ are found by using the relation

$$\theta = \tfrac{8}{9}E_0/R$$

[7] F. Simon and H. E. Megaw, Nature **138**, 244 (1936).

[8] K. Clusius and E. Bartholomé, Zeits. f. physik. Chemie **B30**, 250 (1935).

[9] F. Simon and F. Lange, Zeits. f. Physik **15**, 307 (1923).

* In a private communication with Dr. F. G. Brickwedde we were informed that molar volume of HD at the triple point is 21.8 cc and the lattice energy extrapolated to 0°K in 232 cal./mole. These values are in fair agreement with the values predicted. The deviations would be somewhat decreased if a larger value of d were chosen for the E_0 expression. The molar volume should, of course, be corrected to 0°K for comparison with the predicted values. The change from the triple point to 0°K is estimated to be approximately 0.6 to 0.8 cc.

[10] R. B. Scott, F. G. Brickwedde, H. C. Urey and M. H. Wahl, J. Chem. Phys. **2**, 454 (1934).

TABLE I.

	H_2		D_2		HD
	CALC.	OBS.	CALC.	OBS.	CALC.
V(cm³/mole)	23.24	22.65±0.1	19.78	19.56±0.1	20.96
E(cal./mole)	−180.4	−183.4	−280.6	−274.0	−242.6
E_0(cal./mole)	+161.8		+123.3		+140.2
E_{pot}(cal./mole)	−342.2		−403.9		−382.8
K(cm²/kg)(10⁴)	3.98	5.0 ±0.5	2.20	3.3 ±0.7	3.00

where R is the gas constant. The following table shows the comparison of θ values for the different sets of zero point energies:

	H_2	D_2
Scott[10]	142°	101°
Clusius[8]	136°	96°
Present paper	72°	55°
Observed[11]	105°	97°

No particular significance can be attached to the agreement, or lack of agreement of these figures, and especially is this true of our values, as they are arrived at on a basis quite different from the Debye theory.

The value of the zero point energy of D_2 of 123 cal. for the close-packed lattice may well be compared with the value of 34 cal. for diamond lattice of the equal mass molecule He. The higher zero point energy of D_2 corresponds to the smaller uncertainty of location of its molecules. In fact, if the molecules are more definitely located, a higher zero point energy is necessary.

A graphic comparison of He and H_2 has been made in Fig. 2 and Fig. 3, in which we have plotted the total energy E, the negative of the zero point energy, $-E_0$, and the potential energy, E_{pot}, for the close-packed, and diamond structure

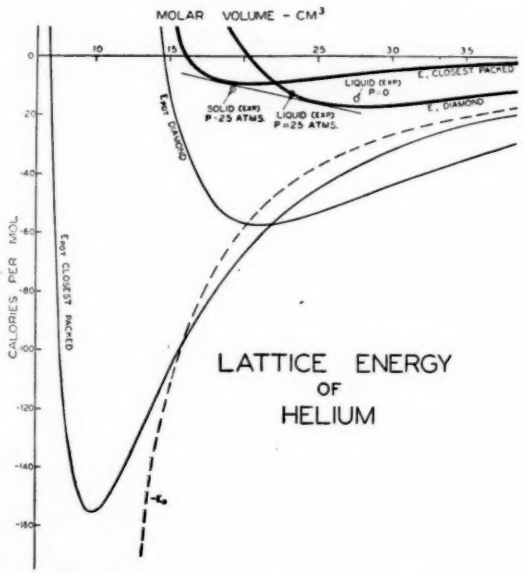

FIG. 3. Lattice energy, E, potential energy, E_{pot}, and the negative of the zero point energy, $-E_0$, for the face-centered cubic, and diamond lattices of He.

[11] A. Eucken and E. Bartholomé, Zeits. f. Elektrochem. **42**, 547 (1936).

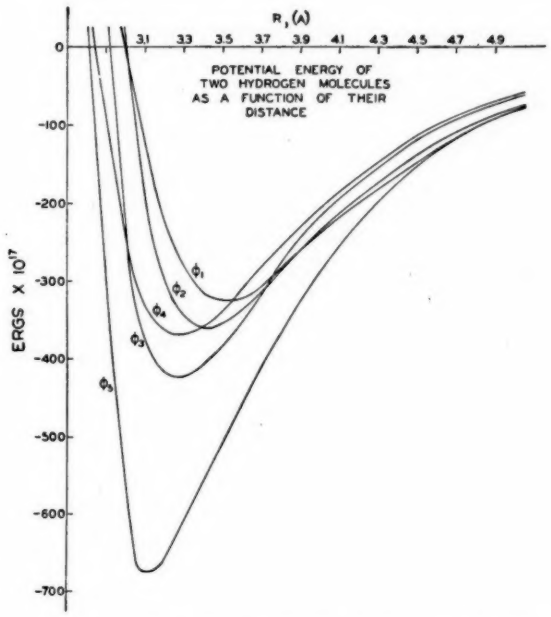

FIG. 4. Different potential energy functions of two interacting H_2 molecules. ϕ_1, ϕ_2, ϕ_3 by Lennard-Jones; ϕ_4 by Bijl, and ϕ_5 by Wohl.

of H_2 (Fig. 2) and He (Fig. 3). The data for Fig. 3 were taken from L. The same E_0 expression with proper masses and d values, has been used for H_2 and He. One sees that in He, in contrast to H_2, the closest packed structure is not the most stable configuration. This has some bearing on the fact that He remains a liquid in the absence of external pressure, whereas H_2 solidifies under its own vapor pressure at 13.95°K.

In conclusion we may briefly diseuss other expressions proposed for the interaction potential energy of two H_2 molecules. (See Fig. 4.) As previously mentioned, Lennard-Jones[4] gives three functions, (ϕ_1, ϕ_2, ϕ_3 below), obtained by adaptation of the energy function to fit the second virial coefficient. Bijl[12] has already discussed solid H_2 and D_2 using a function (ϕ_4) based on a rather doubtful adaptation to H_2 of the Slater and Kirkwood[13] function for He. Wohl[14] proposes a function (ϕ_5) taking as a basis a theoretical value of the attractive coefficient $\sim R^{-6}$ and arriving at the repulsion term by means of the empirical gas equation.

[12] A. Bijl, Physica **4**, 329 (1927).
[13] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
[14] K. Wohl, Zeits. f. physik. Chemie **B14**, 63 (1931).

Lennard-Jones $\phi_1=\left(\frac{51}{r^9}-\frac{1.78}{r^6}\right)10^{-11}$ erg.

$\phi_2=\left(\frac{116}{r^{10}}-\frac{1.42}{r^6}\right)10^{-11}$ erg.

$\phi_3=\left(\frac{649}{r^{12}}-\frac{1.05}{r^6}\right)10^{-11}$ erg.

Bijl $\phi_4=\left(113e^{-3.37}-\frac{1.30}{r^6}\right)10^{-11}$ erg.

Wohl $\phi_5=\left(\frac{29.1}{r^9}-\frac{1.22}{r^6}\right)10^{-11}$ erg.

(r in A)

As may be seen in Fig. 4, ϕ_1 and ϕ_2 are not very different from each other, and actually yield about the same agreement for the energy and volume of solid H_2 and D_2. The agreement using ϕ_3 is not particularly good. All three of these are, of course, based on experimental data for H_2. Bijl's expression, ϕ_4, is based on a theoretical calculation of the r^{-6} term and the use of the mentioned analogy with He for the repulsive term. Wohl's function, ϕ_5, was determined by using the London expression for the numerator of the attractive term. This term is too small as is to be expected since the London expression gives, if only the r^{-6} term is considered, too small a value for the attraction. In view of this one might anticipate that the repulsion in ϕ_4, and ϕ_5 is assumed too small, since it has to compensate for too small an attraction. Accordingly ϕ_4 and ϕ_5 give only very poor agreement with experiment. ϕ_1 is so closely related to the experimental observation as to inspire confidence in its use. The use of the same Lennard-Jones equation for D_2, H_2 and HD may be open to some objections, as for example those suggested theoretically by Beth and Uhlenbeck.[15] However, it is felt that the results obtained are in such close agreement with experiment that one may consider the above procedure as justified for H_2 and as a reasonable approach for HD and D_2.*

ACKNOWLEDGMENT

The author wishes to thank Dr. F. London for suggesting this problem, and for his many helpful discussions during its progress.

[15] R. Beth and G. Uhlenbeck, Physica **3**, 729 (1936).

* In this connection see the reports by K. Schafer (Naturwiss. **24**, 539 (1936); Zeits. f. physik. Chemie **B36**, 85 (1937); **B38**, 187 (1937)) on the second virial coefficients of H_2 and D_2.

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Density of Single Crystals of Cupric Acetate Monohydrate

S. S. SIDHU AND J. A. BERGER
The Cooperative X-Ray Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania

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Densities of single crystals of cupric acetate monohydrate have been determined by the pycnometer method for temperatures 21.0°C, 23.5°C and 25.0°C, and are 1.907 ± 0.001, 1.891 ± 0.004 and 1.880 ± 0.003 g cm^{-3}, respectively. The first one compares favorably with the value (1.906 g cm^{-3}) calculated at about 21.0°C from accurately determined lattice parameters of the unit cell and the number of molecules per unit cell. It is considerably higher, however, than the value (1.882 g cm^{-3}) given in the *International Critical Tables.*

I. INTRODUCTION

FROM accurately determined values of the lattice parameters[1] of the unit cell of copper acetate monohydrate, the volume of the elementary cell was found to be $1379\pm0.04\times10^{-24}$ cc. Taking the value of density for this substance from the *International Critical Tables*[2] as 1.882 g cm^{-3}, the number of molecules per unit cell was calculated as 7.90. This value, though sufficiently close to indicate that there are eight molecules per unit cell, gave a discrepancy which was too large for an experimental error in the

[1] R. B. Hull, Thesis for the degree of Doctor of Philosophy, University of Pittsburgh, 1938.

[2] *Int. Crit. Tab.* (McGraw-Hill, New York), Vol. 1, p. 123.

determination of the lattice parameters. Therefore, it was decided to determine experimentally the value of the density of single crystals of copper acetate monohydrate similar to those used for the x-ray study.

Growth of the crystals from dilute solution

The crystals were grown from a dilute solution of Mallinckrodt analytic reagent grade copper acetate. The solution was filtered three times, poured into a clean porcelain dish with free acetic acid and allowed to evaporate slowly on a steam radiator at a temperature of approximately 33°C. In about fifteen hours good sized, dark, blue-green crystals were taken out of the dish. An attempt was also made to grow single crystals from saturated solutions of copper acetate, but the crystals thus obtained were too small and were considered unsatisfactory for this work.

II. Experimental Procedure

Determination of specific gravity was made by the pycnometer method. The crystals were well dried and polished with lens paper before weighing. Small pycnometers were chosen to eliminate the buoyancy effect due to the net volume of air displaced. The outer volume of the pycnometer including the plug was 14.0 cc; and the volume of the weights used varied from 1.5 to 2.0 cc. The buoyancy effect of the air displaced (12.0 to 12.5 cc) was well within the experimental error.

In determining the weight of the pycnometer filled with the crystals and oil, the crystals were well shaken when immersed, to eliminate any air bubbles adhering to them. The pycnometer was kept in an ice bath for 45 minutes before transferring to a constant temperature calorimeter bath. The temperature of the latter was higher than that of the ice bath; hence, the oil on expansion expelled any air which might have been present in the capillary of the pycnometer plug. Similar procedure was followed in obtaining weights of pycnometer filled with oil and filled with water alone. White Russian mineral oil (specific gravity 0.861 at 21.0°C) was found to be a convenient nonsolvent for these determinations.

The temperature of the calorimeter bath was regulated at 21.0°C and 23.5°C and 25.0°C, and measured by a thermometer that was calibrated from one, certified by the National Bureau of Standards. The room temperature was kept practically the same as that of the calorimeter bath.

Table I. *Density of single crystals of copper acetate monohydrate.*

Temperature °C	Specific Gravity	Density g cm^{-3}
21.0	1.911±0.001	1.907±0.001
23.5	1.896±0.004	1.891±0.004
25.0	1.886±0.003	1.880±0.003

III. Results

In Table I are given the values of specific gravity and the corresponding values of density. The final values together with mean deviations presented here were obtained from the average of three readings taken at each temperature.

The diffraction patterns of single crystals from which the lattice parameters were obtained were made at about 21.0°C. Using 1.907 grams per cc as the density and Hull's value of $1379\pm0.04 \times 10^{-24}$ cc as the volume of the elementary cell, the number of molecules per unit cell has been calculated as follows:

$$\text{Mass per cell} = 1.907\ \text{g/cm}^3 \times 1379 \times 10^{-24}\ \text{cm}^3$$
$$= 2630 \times 10^{-24}\ \text{g}.$$

$$\text{Mass per molecule} = \frac{\text{Mole wt. of copper acetate} \times \text{mass of H atom}}{\text{Mole wt. of hydrogen}}$$
$$= \frac{199.632 \times 1.659 \times 10^{-24}\ \text{g}}{1.0078}$$
$$= 328.6 \times 10^{-24}\ \text{g}.$$

$$\text{No. molecules per cell} = \frac{\text{mass per cell}}{\text{mass per molecule}} = 8.00.$$

This value agrees very well with the actual value of 8. The value of the density used in this calculation compares favorably with the value of 1.906 g cm^{-3} calculated at 21.0°C. It is higher, however, than the two other values obtained here, and also the value given in *The International Critical Tables*.[2]

Dissociation Treatment of Condensing Systems*

WILLIAM BAND
Yenching University, Peiping, China
(Received March 6, 1939)

INTRODUCTION

FOWLER[1] pointed out that imperfect gas theory can be treated as a problem in dissociation, but expressed a doubt as to whether this method would work out so conveniently as did Ursell's at fairly high concentrations. However the success of Mayer's[2] work using the existence of a most probable type of clustering dependent upon temperature, suggests that the dissociation method might be more effective than at first appeared. Mayer's general results in fact can be derived almost immediately from the theory of dissociating assemblies, thus avoiding much of his preliminary argument. Fowler's general method[3] for gaseous assemblies with any number of components and any number of reactions is at once applicable to a gas of *one* component and any number of reactions—clustering processes or collisions. The dissociating molecule of type s is now a cluster of s atoms. Fowler's Eqs. (479) and (484), giving the law of mass action and the external pressure exerted by the gas, are, with classical partition functions, almost obviously identical with Mayer's Eqs. (43) and (37) when recast into the notation there used. The dissociation treatment moreover leads to a much more tractable method of attacking actual cases than that used by Mayer and Ackermann.[4]

DISSOCIATION THEORY

Consider a classical assembly of molecules forming an imperfect gas. The field of force around any molecule will be supposed to be confined within a small volume τ. A cluster of type 2 will be counted as formed whenever two molecules approach each other so closely (i.e., collide) so that the center of either is within the τ of the other. The cluster will be counted as dissociating when the molecules move out of such a range. A cluster of type s is such that every one of the s molecules is linked to every other of them at least indirectly by such interacting pairs. A free molecule will, merely for convenience in notation, be called a cluster of type 1.

Any cluster of given type can change its pattern, and hence its internal energy, in a theoretically enumerable number of ways. The total interaction energy with a cluster of type s may, theoretically, be averaged over these different patterns, and this average may be used in constructing classical partition functions for this type of cluster as one dissociating constituent in the assembly.

The assembly is to be treated as perfect, in the sense that any interaction potential between the clusters is already taken care of in the processes of association and dissociation. Even free molecules do not interact as such, because the occurrence of such interation is merely counted as the appearance of a new cluster of higher type.

Let N be the total number of molecules in the assembly, N_s be the number of clusters of type s in any particular example of the assembly. Then

$$N=\Sigma sN_s. \tag{1}$$

Write $f_s(T)$ for the partition function of the cluster of type s, then Fowler's Eq. (479) immediately reduces to the following set of relations between the averages of N_s:

$$\bar{N}_s/(\bar{N}_1)^s=f_s(T)/[f_1(T)]^s. \tag{2}$$

Also Fowler's Eq. (484) reduces to the following expression for the external pressure exerted on the gas:

$$PV=kT\Sigma\bar{N}_s. \tag{3}$$

Introducing Mayer's notation[2]

$$\mu_s=N_s/N, \qquad \mu=\Sigma'\mu_s$$
$$\lambda=(N-N_1)/N=\Sigma' s\mu_s, \tag{4}$$

where Σ' means sum from $s=2$; the law of mass

* Contribution from the Physics Department, Yenching University.

[1] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1936), §9.6.

[2] J. E. Mayer, J. Chem. Phys. **5**, 67–74 (1937).

[3] Reference 1, §5.3.

[4] J. E. Mayer and P. G. Ackermann, J. Chem. Phys. **5**, 74–83 (1937).

action becomes

$$\bar{\mu}_s/(1-\bar{\lambda})^s = N^{(s-1)} f_s(T)/[f_1(T)]^s. \quad (5)$$

From (4) we can also write this as

$$\bar{\lambda}/(1-\bar{\lambda}) = \sum' s N^{(s-1)} (1-\bar{\lambda})^{(s-1)} \times f_s(T)/[f_1(T)]^s. \quad (6)$$

If from this point on, no further use is made of the idea of clusters, the result (6) reduces to precisely the same as Mayer's. For in this case the partition function for the cluster of type s is merely that for an assembly of s atoms possessing interaction energy:

$$f_s(T) = V(2\pi mkT)^{(3s/2)} h^{(-3s)} b(s, T), \quad (7)$$

where

$$b(s, T) = \frac{1}{s!} \int \cdots \cdots \cdots \int_{\text{cluster}} \exp(-W_s/kT) dq_1 \times \cdots dq_{3(s-1)}. \quad (8)$$

Here W_s is the total interaction energy of the cluster, and the integrals have to be taken only over those regions in phase coordinate space in which the cluster remains a cluster of the given type s. By the trick of substituting $[\exp(-W_s/kT)-1]$ for $\exp(-W_s/kT)$ these integrations can be extended over the whole space, provided the volume of the cluster itself is neglected; substituting (7) and (8) into (6) Mayer's Eq. (43) is at once produced. This shows that Mayer's result follows as a special case of dissociation theory; our Eq. (6) will permit use of other than classical partition functions, in a manner which could not have been assumed from the arguments employed in Mayer's work.

Condensation as a Clustering Process

If at the point, Eq. (6), the physical meaning of a cluster is made use of, considerable simplification of the ensuing computations is effected; greater physical insight is also gained by this method of attack.

In the previous method, call it the pure collision method, the kinetic and potential energies are treated separately. While rigorously correct, this separation is responsible for the neglect of an important distinction between binary and higher order collisions. During an elastic collision between two atoms there is necessarily produced kinetic energy equal and opposite to any decrease in potential energy of interaction, and no stable cluster can be formed. All imperfect gas theory, prior to Mayer's work, appears to assume that higher order collisions are of the same kind but of negligible frequency, and hence omits them from the analysis. But, as soon as the possibility of ternary collisions is admitted, actually stable clusters of type two are possible of a lifetime almost indefinitely long compared with the duration of a simple binary collision. Their effect is therefore very much greater than their frequency of formation would suggest, and it is definitely wrong to suppose that they can be neglected in comparison with elastic binary collisions. In fact their presence is accounted for in the pure collision method, because all kinetic energies are associated with every potential energy; but the method conceals their presence by a mathematical trick.

In fact with a Maxwell distribution over kinetic energies the more stable clusters are the more probable, and a good approximation to the truth would be secured by assuming that pure binary collisions are in fact of negligible importance compared with stable binary clusters. This is exactly the opposite of the assumption that comes most easily from a pure collision point of view.

The condensed phase of the assembly is now to be regarded as that condition in which the whole assembly is in one single cluster, $N_s=1$, $s=N$. The latent heat of the phase change is to be identified with the energy which must be removed in order to reduce to a stable cluster what would otherwise be a mere transitory collision involving the whole assembly. This energy removal cannot consistently be supposed to take place only at the formation of the final grand cluster; it is a general feature of clusters of all types, and occurs continually as clustering progresses, e.g. during a decrease in the volume of a vapor. It is merely because there is, as shown by Mayer, a critical molecular volume at which clustering rapidly becomes important, that latent heat also appears to be removed only

at one definite temperature. From this point of view the heat loss during the Joule-Thomson porous plug experiment gives the latent heat curve at temperatures above boiling point.

Saturated Vapor Equations

Considering a cluster of type s simply as a single "molecule" or system of mass ms, its partition function will be, instead of (7):

$$f_s(T)=V(2\pi mskT)^{(3/2)}h^{-3}\exp\left(-\overline{W}_s/kT\right), \quad (9)$$

where $\overline{W}_s$ is the mean internal energy of such clusters. This must include all negative energy of interaction between the a atoms, and all "internal" kinetic energy. The latter will be assumed proportional to $(s-1)$, will actually have the mean value $3/2kT(s-1)$ for a Maxwellian distribution. The interaction energy will also be nearly proportional to $(s-1)$, but there will be a correction term due to surface energy which will increase less rapidly than s. Therefore write:

$$\overline{W}_s=W(s-1)+\chi(s,T), \quad (10)$$

where

$$\chi(s,T)\ll W(s-1), \text{ large } s. \quad (11)$$

Also from the physical meaning of $\overline{W}_s$ it is necessarily true that

$$\chi(1,T)=0. \quad (12)$$

Using these results in (9) for the partition function, the equation of mass action (6) becomes:

$$\frac{\bar{\lambda}}{1-\bar{\lambda}}=\sum{}'s^{5/2}e^{-\chi/kT}\left\{\frac{h^3e^{-W/kT}(1-\bar{\lambda})}{(2\pi mkT)^{3/2}V/N}\right\}^{(s-1)}. \quad (13)$$

As in Mayer's work, there will be a critical value $\bar{\lambda}_c$ of $\bar{\lambda}$ when

$$V_c/N=h^3(2\pi mkT)^{-3/2}(1-\bar{\lambda}_c)e^{-W/kT}, \quad (14)$$

where

$$\bar{\lambda}_c/(1-\bar{\lambda}_c)=\sigma=\sum{}'s^{5/2}e^{-\chi/kT}. \quad (15)$$

Similarly, from (5) the critical value $\bar{\mu}_c$ of $\bar{\mu}$ can be derived:

$$\bar{\mu}_c/(1-\bar{\lambda}_c)=\phi=\sum{}'s^{3/2}e^{-\chi/kT}. \quad (16)$$

Using (4) at the saturation point given by (14), (15) and (16), we have the equations for the saturated vapor in the form:

$$P_cV_c=NkT(1+\phi)/(1+\sigma). \quad (17)$$

It is remarkable that this $P-V$ curve depends through the sums (15) and (16) only upon the *surface* energy of the clusters.

The essential advantage of this method of attack over that of Mayer and Ackermann[4] is that the computational difficulties are resolved into two separate problems. In the first problem, outlined above, it is proposed to obtain, from the properties of saturated vapor, information on surface energies of clusters of vapor molecules. In the second problem this information would be used in a study of molecular force fields.

A rough check on the properties of water vapor has shown the orders of magnitude correct. The detailed analysis is now being attempted.

The writer wishes to thank Professor R. H. Fowler for introducing him to this subject.

Optical Activity of the Sugars

EVERETT GORIN, WALTER KAUZMANN AND JOHN WALTER
Frick Chemical Laboratory, Princeton University, Princeton, New Jersey
(Received December 28, 1938)

The optical activities of some pentose sugars have been calculated by using the one-electron theory. The relative signs calculated agree in every case with those experimentally observed while the agreement as to magnitude is satisfactory. Some general considerations concerning the superposition rules are presented. It is shown that the rule is derivable upon the basis of the additivity of the vicinal effects. In addition certain requirements on the structure of the pyranose ring must be fulfilled.

INTRODUCTION

IN a previous paper[1] a method of calculating optical activity on a quantum mechanical basis was developed and applied to *sec*-butyl alcohol. This method was an extension of the one-electron point of view first proposed by Condon, Altar and Eyring.[2] It has seemed desirable to extend this treatment to more complicated molecules in order to determine its validity and to investigate further its value in the determination of absolute configuration. Because the configuration of the sugars relative to *sec*-butyl alcohol is known,[3] and because of their importance in structural chemistry, we have chosen the sugars for this work.

All the electronic transitions in a molecule contribute to the optical activity in the visible, but from an experimental point of view[4] the sign and magnitude of the rotation is determined by the transitions corresponding to one or more of the absorption bands nearest the visible. These absorption bands can usually be identified with certain so-called chromophoric groups in the molecule. On the basis of the one-electron picture used here, these transitions are attributed to a single-electron jump largely localized in the chromophoric group. In the case of *sec*-butyl alcohol, the optical activity was attributed to the complex absorption band of the hydroxyl group[5] lying at 1700A. The optical activities of the sugars should also be determined largely by optical transitions in the hydroxyl groups since their characteristic absorption bands lie closest to the visible. As a matter of fact, the optical dispersion of sugars is very nearly simple in most cases and has a dispersion constant very nearly the same as in secondary alcohols. These considerations make the extension of the calculations to the sugars a relatively simple matter.

METHOD OF CALCULATION

The method as applied to the pentose sugars was identical with that applied in the previous treatment of *sec*-butyl alcohol. The chromophoric electrons were assumed to be the nonbonding electrons on the various oxygen atoms, and the matrix components $(a|\mathbf{p}|b)$ and $(a|\mathbf{m}|b)$ evaluated by considering the chromophoric electron to be moving in the Hartree field of the other atoms of the molecule. The potentials due to the hydrogen, carbon and oxygen atoms were evaluated by the use of Slater-type eigenfunctions. These were found to be:

$$V_{H(i)} = -\frac{e^2}{a_0}\left(1+\frac{a_0}{r_i}\right)\exp\left(-\frac{2r_i}{a_0}\right),$$

$$V_{C(i)} = -4\frac{e^2}{a_0}\left(1.070\frac{r_i^2}{a_0^2}+2.175\frac{r_i}{a_0}+2.213+\frac{a_0}{r_i}\right)\exp\left(-\frac{2.95r_i}{a_0}\right),$$

[1] E. Gorin, J. Walter and H. Eyring, J. Chem. Phys. **6**, 824 (1938).
[2] E. Condon, W. Altar and H. Eyring, J. Chem. Phys. **5**, 753 (1937).
[3] W. Kuhn, Naturwiss. **20**, 20 (1938).
[4] P. A. Levene, Gilman's *Treatise on Organic Chemistry*, Vol. II, p. 1779.
[5] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 390 (1930).

$$V_{O(i)}=-\frac{e^2}{a_0}\left(19.19\frac{r_i^2}{a_0^2}+27.09\frac{r_i}{a_0}+19.13+\frac{6a_0}{r_i}\right)\times\exp\left(-4.25\frac{r_i}{a_0}\right)-\frac{e^2}{a_0}\left\{\left(19.75\frac{r_i^2}{a_0^2}+22.56\frac{r_i}{a_0}+21.25+15\frac{a_0}{r_i}+7.059\frac{a_0^2}{r_i^2}+1.661\frac{a_0^3}{r_i^3}\right)\exp\left(-4.25\frac{r_i}{a_0}\right)-1.661\frac{a_0^3}{r_i^3}\right\}\times\{\tfrac{3}{5}\sin^2\theta_i\cos^2\varphi_i-\tfrac{1}{5}\},$$

where r_i, θ_i, and φ_i are the coordinates of the chromophoric electron relative to the ith atom. The yz plane in the case of the oxygen potential is the plane of the COH or COC to which the ith oxygen atom belongs. This determines the angular factor.

The electronic transition is assumed to be from the initial $2p_x$ state of the nonbonding oxygen electron to the three excited states corresponding to the proper linear combinations of the $3s$, $3p_y$ and $3p_z$ states of oxygen,

$$\text{Excited states } \psi_n'=C_{n2}\psi_{3s}+C_{n3}\psi_{3p(y)}+C_{n4}\psi_{3p(z)}\quad n=1,\ 2,\ 3.$$

The coefficients C_n are the same as those obtained previously for the COH group. For the ether oxygen in the pyranose ring the linear combination was taken to be that which is proper for the COC group. The y and z axes were so chosen as to lie in the COC plane and to make equal angles with the O−C bond directions. We thus obtain two functions which are even with respect to reflection in the plane bisecting the COC angle and one which is odd with respect to this reflection. The three zero-order functions are therefore:

$$\psi_1'=\psi_{3s},\quad \psi_2'=\frac{\psi_{3p(y)}+\psi_{3p(z)}}{\sqrt{2}},\quad \psi_3'=\frac{\psi_{3p(y)}-\psi_{3p(z)}}{\sqrt{2}}.$$

The transitions are made optically active by the perturbing action of atoms outside of the chromophoric group which combines even states with odd states. Thus the excited states become:

$$\chi_n=C_{n5}\psi_{2p(y)}+C_{n6}\psi_{2p(z)}+\psi_n'+C_{n7}\psi_{3d(xz)}+C_{n8}\psi_{3d(xy)}.$$

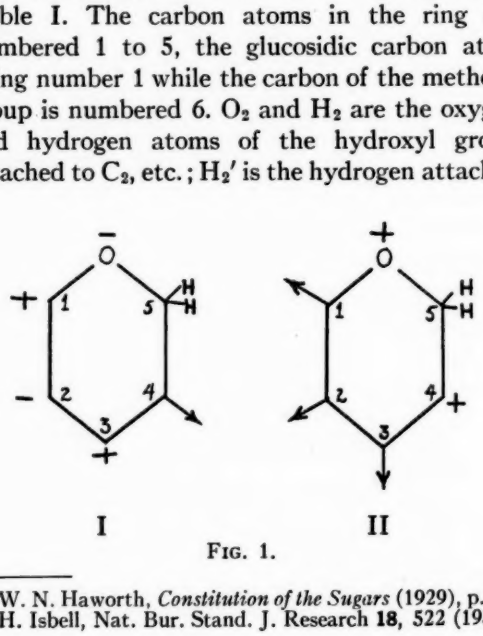
The molecular optical activity parameter β is then calculated to be:

$$\beta=\frac{e^2a_0}{12\pi^2m}\frac{1}{\nu_n^2-\nu^2}\left(\int\psi_{3d(xy)}Y\psi_{2p(x)}d\tau\right)\times(C_{n5}C_{n8}-C_{n6}C_{n7}),$$

where $n=1$, 2, 3, and ν_n is the frequency corresponding to the transition from the normal state to the nth excited state.

Conformation and Orientation

The pyranose ring, as is well known, has several possible conformations.[6] In particular there are two possible chair forms,[7] and numerous possible boat forms, if the angles are tetrahedral. Because of the somewhat laborious nature of the calculations it was not deemed feasible to calculate all the possibilities, and we have concentrated our attention upon the conformation that seemed most probable. The boat forms would seem to be unstable due to large repulsions both in the ring and among the subsidiary groups. The two possible chair forms of *d*-α methyl arabinopyranoside are illustrated schematically in Fig. 1. We have based our calculations on conformation I. The question of the conformation of the ring will be discussed later in more detail. The coordinates of chair form I are given in Table I. The carbon atoms in the ring are numbered 1 to 5, the glucosidic carbon atom being number 1 while the carbon of the methoxy group is numbered 6. O_2 and H_2 are the oxygen and hydrogen atoms of the hydroxyl group attached to C_2, etc.; H_2' is the hydrogen attached



I II

FIG. 1.

[6] W. N. Haworth, *Constitution of the Sugars* (1929), p. 90.
[7] H. Isbell, Nat. Bur. Stand. J. Research **18**, 522 (1937).

directly to C_2, etc. The pyranose oxygen is numbered 5, and is below the plane of C_1, C_2, C_4, C_5. The groups on C_1 and C_3 are pointing up from the ring, the group on C_2 is pointing down from the ring, and the group on C_4 is pointing away from the ring and slightly upward. The center of coordinates is fixed in C_3 with the axes so chosen that O_3 is in the direction of the $+++$ diagonal of a cube about C_3 as a center. All carbon valence angles were taken to be tetrahedral. The oxygen valence angle was taken as 105°.

It remains to fix the orientation of the hydroxyl groups about the C−O bond. Hudson's rules indicate either that there is free rotation of the hydroxyl groups or that their orientations are unaffected by the configurations of the hydroxyl groups about neighboring carbon atoms. The possibility of free rotation is ruled out by recent evidence[8] which indicates a potential barrier of the order of 10,000 cal. for the rotation about the C−O bond in methyl alcohol. We consider that the cause of this restricted rotation is due to the interaction of the dissymmetric charge distribution on the oxygen atom with a dissymmetry induced in the carbon atom by the bonds which it forms with the two carbon atoms in the ring and the attached hydrogen atom. This dissymmetry is caused by a concentration of charge along the

TABLE I. *Coordinates of d-α-methyl arabinopyranoside.*

	C_1	C_2	C_3	C_4	C_5	O_5	O_1	C_6	H_1'
x	0.00	−0.89	0.00	+0.89	+1.62	+0.67	+0.94	+0.68	−0.62
y	+1.62	+0.89	0.00	−0.89	0.00	+0.67	+2.43	+3.76	+2.25
z	−1.92	−0.89	0.00	−0.89	−1.92	−2.73	−1.24	−1.68	−2.56

	O_2	H_2	H_2'	O_3	H_3	H_3'	O_4	H_4	H_4'	H_5'	H_5''
x	−1.84	−2.70	−1.41	+0.82	+0.60	−0.63	+1.84	+1.66	+0.29	+2.22	+2.25
y	+0.09	+0.44	+1.62	+0.82	+0.60	−0.63	−1.57	−2.51	−1.62	+0.72	−0.62
z	−1.57	−1.28	−0.29	+0.82	+1.73	+0.63	−0.09	−0.23	−1.41	−1.40	−2.56

bond directions. Consequently the positions of minimum potential will be where the angle between the nonbonding oxygen orbit and the carbon valence directions would be a maximum. This would correspond, if all three directions were equivalent, to an orientation such that the COH plane bisects the angle of any two of the three bond directions. Since the C−H bond is the strongest we might expect to have the strongest accumulation in this direction, and therefore the most stable position will be that where the COH plane bisects the C−C−C valence angle. This leaves either of two possible orientations. Since if the hydroxyl hydrogen were directed outward from the ring the repulsions between the hydroxyls would be minimized, we have chosen this to be the most probable orientation for all the hydroxyls. This corresponds to our orientation II in *sec*-butyl alcohol. The calculation of the contribution due to each chromophoric electron, of course, requires that a transformation be made to a new coordinate system such that the yz plane corresponds to the plane of the chromophoric group and that the new coordinate center corresponds to the center of gravity of the chromophoric electron in question.

TABLE II.

V_c			V_0(sym)			V_0(unsym)	
R	$3p3d$	$3s3d$	R	$3p3d$	$3s3d$	$3p3d$	$3s3d$
2.43	2.083	− .884	2.234	1.565	−.606	.280	−.108
2.53	2.167	− .967	2.70	1.644	−.720	.214	−.129
2.95	2.012	−1.030	3.60	1.058	−.630	.189	−.113
3.28	1.768	− .992	4.30	.544	−.349	.097	−.062
3.49	1.524	− .881					
3.82	1.187	− .720					
4.41	.686	− .438					
5.69	.135	− .092					

Since we were only interested in the sign and order of magnitude of the rotation the perturbing action of the hydrogen atoms outside the COH groups were neglected. These perturbations are in any case small in comparison to those due to the carbon and oxygen atoms. For this reason the coordinates of the hydrogen atoms on the methyl group are not included in Table I.

RESULTS

In calculating the coefficients C_{n5}, C_{n6}, C_{n7} and C_{n8} it is necessary to know the values of some integrals not given in Table II of our previous paper. These are given here in Table II. The integrals $3p3d$ and $3s3d$ are the numerical factors in the integrals $\int\psi_2 V\psi_7$ and $\int\psi_4 V\psi_7$ of the preceding paper. These must be multiplied by the usual factors depending upon γ_1, γ_2, and γ_3. In addition the numerical factor due to the

[8] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 480 (1938).

unsymmetrical part of the oxygen potential must be multiplied by a factor $(1-\gamma_1'^2)$. γ_1' is the direction cosine of the chromophoric oxygen with respect to the fixed axes in the perturbing oxygen, while γ_1, γ_2, γ_3 are the usual direction cosines with respect to the axes fixed in the chromophoric oxygen.

The partial contributions of the various chromophoric oxygen atoms along with the total rotatory parameter β are given in Table III.

We see that the sign is in every case correct and the agreement as to order of magnitude is as good as could be expected considering the number of approximations made. It is interesting to note that although the vicinal effects of the hydroxyl groups on one another are fairly large, Hudson's rules are very nearly valid. Thus the difference in the rotatory parameters for α and β arabinopyranoside is 1.89×10^{-34}, and for α and β lyxopyranoside it is 1.75×10^{-34}. It is observed, however, that sugars of the lyxose sugars do not obey Hudson's rules. The fact that our calculations with a fixed conformation of the ring shows that Hudson's rules should be obeyed may indicate that the form of the ring is considerably modified in the lyxose sugars.

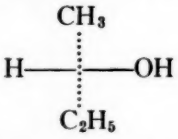
It is further noted that the signs of the various partial contributions of the chromophoric oxygen atoms agree with the signs assigned by sugar chemists[9] to the partial rotations of the various asymmetric carbon atoms in the pentose sugars. The greatest discrepancy is in the magnitude of the contribution of the glucosidic oxygen, which is only one-third as large as would be expected. By a direct application of the superposition rule we find for the glycosides of α- and β-xylose the values $+1.60\times10^{-34}$ and -0.51×10^{-34} for the molecular rotatory parameter as compared with the observed values $+4.0\times10^{-34}$ and -1.9×10^{-34}.

Table III.

α-Methyl Arabino-pyranoside	β-Methyl Arabino-pyranoside	α-Methyl Lyxo-pyranoside	β-Methyl Lyxo-pyranoside
O_1 $+0.87\times10^{-34}$	-0.94×10^{-34}	$+0.50\times10^{-34}$	-1.02×10^{-34}
O_2 $-$ .27	$-$ .40	$-$ .34	$-$ .47
O_3 -1.06	$-$ .82	$+$ .58	$+$ .67
O_4 $-$ .67	$-$ .67	$-$ .09	$-$ .09
O_5 $+$ .07	$-$ .12	$+$ .07	$-$ .12
β_{calc} -1.06×10^{-34}	-2.95×10^{-34}	$+$ .72$\times10^{-34}$	-1.03×10^{-34}
β_{obs} $-$ .46$\times10^{-34}$	-6.4×10^{-34}	$+1.5\times10^{-34}$	(-3.0×10^{-34})‡

‡ Calculated from Hudson's rules.

In the previous paper we assigned the following absolute configuration to *d-sec*-butyl alcohol.



This was found to rotate positively. Now it has been found experimentally that *d*-secondary butyl alcohol is related configurationally to *d*-arabinose. Therefore the absolute configuration to be assigned to *d*-arabinose is the one we have used for our calculations. Since experimentally *d*-secondary butyl alcohol rotates positively and *d*-arabinose rotates negatively, the calculated values for the two compounds should be of opposite sign. This is found to be the case. The consistency of our results with regard to sign therefore allows us to place some confidence in the absolute configuration of secondary butyl alcohol given above.

Our calculations have shown that it is reasonable to assume that Hudson's rules are derivable from the one-electron theory. We now proceed to investigate a proof of Hudson's rules based upon more general considerations.

Optical Superposition

Van't Hoff's explanation of the existence of optically active substances, centering attention as it did upon the asymmetric carbon atom, gave rise to the concept of optical superposition. The more recent recognition of optical activity as a function of molecular asymmetry should have disposed of this concept, however, and although the development of the idea of a partial rotation by each of the groups of the molecule might lead one back to van't Hoff's attitude, this must finally be rejected when it is realized that the partial rotation of a group is a function of that group's interactions with the rest of the molecule —a fact which is the prime feature of all modern theories of optical activity. That these interactions should merely change their signs when there is a change in the configuration about one asymmetric center in a molecule containing several such centers is highly improbable[10] unless

[9] H. Isbell, Nat. Bur. Stand. J. Research **3**, 1041 (1929).

[10] G. Read, Trans. Faraday Soc. **26**, 442 (1930).

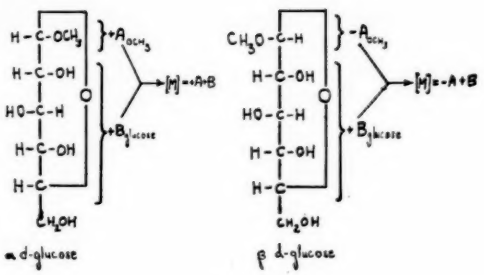


FIG. 2.

only those atoms directly attached to the center can interact. If this last were true, it is readily seen that nearly all known optically active organic compounds would be inactive.[11]

It is, therefore, quite surprising that there should be well-defined instances in which the principle of superposition appears to be true to within at least a close approximation. Outstanding among these are certain derivatives in the field of the carbohydrates to which may be applied the so-called rules of iso-rotation developed by Hudson; since a large amount of data is available here, and because the rules are of importance in carbohydrate chemistry, we shall devote most of our attention to them.

Hudson[12] considered the molecular rotation of a sugar to be made up of the algebraic sum of the rotations of its parts—these latter remaining constant in going from one substance to another. Thus the rotation of, say, the methyl glucosides would be calculated as indicated in Fig. 2. How valid this is in general, that is, for example, how constant A_{OH} remains in the free sugars, and how constant $B_{glucose}$ remains in going from one glucose derivative to another, is at once apparent from an inspection of Table IV. There are, however, notable exceptions, and with these we are to be particularly concerned.

Hudson[13] has shown that a different application of his rules leads to far better results than do the rules in the form originally proposed. This leads us to a *corollary to Hudson's rules* whose form is self-evident from Table V. It should be noted that this corollary is a quantitive illustration of the displacement rule of Kuhn and Freudenberg.[14]

A. A proof of optical superposition

We now present a proof of Hudson's rules in more modern terms which may be directly extended to the general problem of superposition. The proof will be found to impose several conditions on the structures of the sugars and in general on any theory which seeks to explain the optical activity of the sugars.

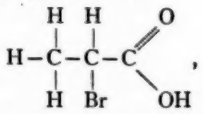
Consider four compounds which differ only in the relative configurations of their groups about their respective centers of asymmetry. The various groups in a given compound need not be the same, but corresponding centers of asymmetry in the compounds must be surrounded by the same groups throughout the series. Let the compounds be represented schematically as shown in Fig. 3.

The optical rotations of these compounds can, under certain conditions to be considered later, be represented as the sum of the vicinal interactions between groups taken two at a time. The vicinal interactions will include implicitly all of those interactions which can affect the optical activity, whether this be directly or indirectly.

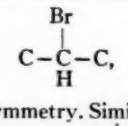
Let $+A_{ij}$ represent the vicinal actions of the ith group helping to give rise to the partial rotation of the jth group when the ith group is on the left and the jth is on the right; and let $-A_{ij}$ represent the same when the ith group is on the right and the jth is on the left.

Let $+B_{ij}$ represent the same when the ith group is on the right and the jth group is on the right; and let $-B_{ij}$ represent the same when the ith group is on the left and the jth group is on the left.

[11] Thus α-bromopropionic acid,



would be inactive since the asymmetric center has two carbon atoms attached to it, so that as far as optical activity would be concerned, it would act like



which has a plane of symmetry. Similarly, the sugars would be inactive since every asymmetric center has either two carbon atoms or two oxygen atoms attached to it.

[12] C. S. Hudson, J. Am. Chem. Soc. **31**, 66 (1909).

[13] C. S. Hudson, J. Am. Chem. Soc. **47**, 271 (1925).

[14] N. A. Sorensen, Det Kgl. Norske Videnskabers Selskabs Skrifter, 1937, No. 2. W. Kuhn, K. Freudenberg, and I. Wolf, Ber. **63**, 2377 (1930).

TABLE IV. *Molecular rotations illustrating Hudson's rules.*

FREE SUGARS (IN H_2O)			METHYL PYRANOSIDES (IN H_2O)		
	$2A_{OH}$ (=diff. in rot. of α and β sugars)	$2B$ (=sum of rot. of α and β sugars)		$2A_{OMe}$	$2B$
l-arabinose	−169.5	+430.5	Methyl *l*-arabinoside	−375.1	+429.9
d-galactose	+172.7	+370.7	Methyl *d*-xyloside	+359.8	+145.0
d-glucose	+169.2	+238.8	Methyl *d*-glucoside	+374.6	+242.0
			Methyl *d*-galactoside	+381.8	+379.0
l-rhamnose	− 84.8	+ 59.6	Methyl *d*-guloside	+392.9	+ 70.9
d-lyxose	+113.3	− 98.6			
d-mannose	+ 83.3	+ 29.5	Methyl *d*-mannoside	+287.2	+ 19.4
d-talose	+ 98.5	+146.5	Methyl *l*-rhamnoside	−281.0	+ 58.6

ACETATES (IN $CHCl_3$)			GLYCOFURANOSIDES (IN H_2O)		
	$2A_{OAc}$	$2B$		$2A_{OR}$	$2B$
Tetracetyl *l*-arabinose	−332.9	+603.3	Methyl *d*-glucoside	+377.9	+79.5
Tetracetyl *d*-xylose	+362.5	+202.9	Ethyl *d*-glucoside	+364.0	+28
Pentacetyl *d*-galactoside (1,5)	+327.0	+513.6	Ethyl *d*-galactoside	+376.5	−19.5
Pentacetyl *d*-galactoside (1,4)	+402.0	+ 34.2	Methyl *d*-mannoside*	+417	+ 1.9
Pentacetyl *d*-glucose	+381.4	+411.1			
Pentacetyl *d*-mannose	+313.0	+117			
Octaacetyl neolactose	+409.8	+313.3			

* E. Pacsu and A. Scattergood, J. Am. Chem. Soc. **61**, 534 (1939).

Let $+A_{jj}$ represent the optical activity of the molecule when all groups but the jth are removed, and when the jth group is on the right, and let $-A_{jj}$ represent the same when the jth group is on the left.

Then the optical activities of the four compounds are given as follows:

I	II
$-A_{11}+A_{12}+A_{13}+A_{14}$	$+A_{11}+B_{12}+B_{13}+B_{14}$
$-A_{21}+A_{22}+B_{23}+B_{24}$	$+B_{21}+A_{22}+B_{23}+B_{24}$
$-A_{31}+B_{32}+A_{33}+B_{34}$	$+B_{31}+B_{32}+A_{33}+B_{34}$
$-A_{41}+B_{42}+B_{43}+A_{44}$	$+B_{41}+B_{42}+B_{43}+A_{44}$

III	IV
$-A_{11}+A_{12}-B_{13}+A_{14}$	$+A_{11}+B_{12}-A_{13}+B_{14}$
$-A_{21}+A_{22}-A_{23}+B_{24}$	$+B_{21}+A_{22}-A_{23}+B_{24}$
$-B_{31}+A_{32}-A_{33}+A_{34}$	$+A_{31}+A_{32}-A_{33}+A_{43}$
$-A_{41}+B_{42}-A_{43}+A_{44}$	$+B_{41}+B_{42}-A_{43}+A_{44}$

Simple subtraction shows that the differences between the optical activities of I and II and of III and IV are:

$$\text{II}-\text{I}=2A_{11}+B_{12}+B_{13}+B_{14}-A_{12}-A_{13}-A_{14}+A_{21}+A_{31}+A_{41}+B_{21}+B_{31}+B_{41}$$

$$\text{IV}-\text{III}=2A_{11}+B_{12}-A_{13}+B_{14}-A_{12}+B_{13}-A_{14}+A_{21}+B_{31}+A_{41}+B_{21}+A_{31}+B_{41}$$

Thus, II − I equals IV − III and we have shown that Hudson's $2A$ must be constant for a series of sugar derivatives meeting the proper requirements.

The extension to the more general case of optical superposition is readily made. Thus, we could remove group 4 and we would find that (I − III − II + IV) is equal to zero, as predicted by the van't Hoff principle of superposition.

The extension of the above to shifts of other groups down the chain[15] is also obvious.

Note that if the alpha-sugar be defined as that sugar of an alpha-beta pair having the higher (more positive) rotation, then all alpha-sugars will have the same configuration about the glucosidic carbon atom. The notation in actual use, however, takes into account the existence of *d*- and *l*-sugars, so that the above statement must be applied to each series separately and in opposite senses.

B. Relationship between Hudson's rules and the corollary to Hudson's rules; constancy of Hudson's 2B; effects of disturbances on the rules

Consider the substances, schematically represented in Fig. 4. There will be the following

[15] H. Isbell, Nat. Bur. Stand. J. Research **18**, 505 (1937).

differences in their optical activities:

$$\text{I}-\text{II}=-A_{2x}+A_{3x}+A_{x2}+A_{x3}+A_{2y}+A_{3y}-A_{y2}-A_{y3}+A_{xx}+A_{yy}$$

$$\text{III}-\text{IV}=B_{2x}+B_{3x}+B_{x2}+B_{x3}+B_{2y}+B_{3y}-B_{y2}-B_{y3}+A_{xx}-A_{yy}$$

$$\text{V}-\text{VI}=-B_{2x}-A_{3x}-B_{x2}+A_{x3}+B_{2y}+A_{3y}+B_{y2}-A_{y3}-A_{xx}+A_{yy}$$

$$\text{VII}-\text{VIII}=A_{2x}+B_{3x}-A_{x2}+B_{x3}-A_{2y}-B_{3y}+A_{y2}-B_{y3}+A_{xx}-A_{yy}.$$

If $A_{2x}-A_{2y}\cong -B_{2x}+B_{2y}$, etc., that is, if $A_{2x}+B_{2x}\cong A_{2y}+B_{2y}$, etc., which is plausible if the group X is similar to the group Y (as is OH to OCH_3), and if $A_{x2}-A_{y2}\cong -B_{x2}+B_{y2}$, etc., that is, if $A_{x2}+B_{x2}\cong A_{y2}+B_{y2}$, etc., which is perhaps a little less plausible than the above under the same conditions, then the corollary to Hudson's rules follows.

The importance of the groups' being similar is indicated by Table VI. Here we are comparing compounds possessing a methoxyl to those containing an acetyl, and since these groups are far from similar, the relatively large irregularity which is observed is understandable.

If, again, groups X and Y are similar, it is readily shown that Hudson's $2B$ should be the same for a sugar in the X series as in the Y series. Thus, $2B$ is the same for the glucoses (α and β) as for the methyl glucosides (α and β), but not for the phenyl glucosides, the phenoxyl group being too different from the hydroxyl and methoxyl. This has been noted by Freudenberg and Kuhn[16] and was explained by them in essentially the same terms as those given above. We might add that there are also relatively large differences between $2B$ for an acetylated methyl glycoside and a completely acetylated sugar, probably for the same reason.

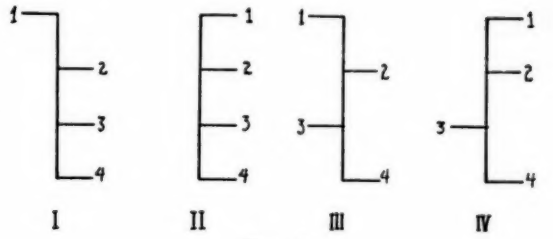


FIG. 3.

Finally, suppose that in I and II some disturbing factor enters which alters A_{2x} to $A_{2x}+e_{2x}$, A_{2y} to $A_{2y}+e_{2y}$, etc. It is readily seen that $2A=(\text{III}-\text{I})$ deviates from the normal $2A$ by an amount $(e_{2x}+e_{3x}-e_{x2}-e_{x3}-e_{xx})$ as compared with $(\text{VII}-\text{V})$, while if $e_{2x}=e_{2y}$, etc., as is reasonable if X and Y are similar, $(\text{I}-\text{II})$ will still equal $-(\text{III}-\text{IV})$ and $(\text{V}-\text{VI})$, etc., so that the modified Hudson's rule will still be true. This appears to be the reason why, when X and Y are similar, the corollary to Hudson's rule holds better than do Hudson's rules themselves.

[16] K. Freudenberg and W. Kuhn, Ber. **64**, 725 (1931).

TABLE V. *Molecular rotations illustrating the corollary to Hudson's rules.*

α-Methyl *d*-glucoside	(+308.3)	$-\alpha$,*d*-glucose (+204)	= +104.3
β-Methyl *d*-glucoside	(− 66.3)	$-\beta$,*d*-glucose (+ 34.8)	= −101.1
α-Methyl *d*-galactoside	(+380.4)	$-\beta$,*d*-galactose (+271.7)	= +108.7
β-Methyl *d*-galactoside	(− 1.4)	$-\beta$,*d*-galactose (+ 99.0)	= −100.4
α-Methyl *d*-mannoside	(+153.3)	$-\alpha$,*d*-mannose (+ 53.9)	= + 99.4
β-Methyl *d*-mannoside	(−133.9)	$-\beta$,*d*-mannose (− 29.4)	= −104.5
α-Methyl *l*-arabinoside	(+ 27.4)	$-\alpha$,*l*-arabinose (+130.5)	= −103.1
β-Methyl *l*-arabinoside	(+402.5)	$-\beta$,*l*-arabinose (300)	= +102.5
α-Methyl *d*-lyxoside	(+ 97.4)	$-\alpha$,*d*-lyxose (+ 8.2)	= + 89.2
α-Methyl *d*-guloside	(+231.9)	$-\alpha$,*d*-gulose (+114.7)	= +117.2

TABLE VI.

α-Methyl *d*-xyloside triacetate	(+347)	$-\alpha$,*d*-xylose tetracetate	(+283) = + 64
β-Methyl *d*-xyloside triacetate	(−176)	$-\alpha$,*d*-xylose tetracetate	(− 79) = − 97
α-Methyl *d*-glucoside tetracetate	(+473)	$-\alpha$,*d*-glucose pentacetate	(+396) = + 77
β-Methyl *d*-glucoside tetracetate	(− 66)	$-\beta$,*d*-glucose pentacetate	(+ 15) = − 81
α-Methyl *d*-galactoside tetracetate	(+484)	$-\alpha$,*d*-galactose pentacetate	(+417) = + 67
β-Methyl *d*-galactoside tetracetate	(− 51)	$-\beta$,*d*-galactose pentacetate	(+ 90) = −141
α-Methyl *d*-mannoside tetracetate	(+178)	$-\alpha$,*d*-mannose pentacetate	(+215) = − 37
β-Methyl *d*-mannoside tetracetate	(−181)	$-\beta$,*d*-mannose pentacetate	(− 98) = − 83

C. Conditions of the proofs

First, that simultaneous reflection of groups i and j shall change the vicinal actions of the first on the second from, say, $+A_{ij}$ to $-A_{ij}$, requires that the skeleton to which the groups are attached (in the sugars, this would mean the ring) have *effectively* a plane of symmetry, and that the groups be attached to it in such a way that shifting a group from one side to the other is equivalent to reflection in that plane. This is a purely structural restriction.

Second, the vicinal actions of pairs of groups must be additive; that is, shifting, say, group No. 2 will not have any effect on the interactions involving groups other than No. 2, e.g., on A_{31}. This is a restriction which must be met both by the theories of optical activity and by those group interactions which can indirectly affect the optical activity, such as forces which tend to orient the hydroxyl about the carbon-oxygen bond in an alcohol.

D. Closer examination of the conditions of the proofs, with particular respect to the sugars

(1) The first condition would be fulfilled in the pyranose sugars (a) if the ring were planar, or (b) if the two possible Sachse chair forms[17] were present in equal amounts, or if the two possible "biplanar" rings[18] were present in equal amounts. In the furanose sugars, the ring is almost certainly planar.

(a) A completely planar pyranose ring seems to be nearly out of the question; it would require a distortion of the valence angles to around 120°, which would in turn require forces all out of proportion to our present ideas of their magnitudes.

It is well to point out here, however, that the ring, even if not perfectly flat, is very possibly more nearly flat than the usual models, employing tetrahedral valence angles, would indicate. There is every indication that the C−C−C bond angle is not tetrahedral: electron diffraction measurements have indicated a deviation of at least one or two degrees in propane. Recently, Beach and Stevenson[19] have found a most probable value of 113½° for this angle in isobutane. Since the spreading of bond angles is undoubtedly caused by the repulsions between the groups concerned, and since the third methyl in isobutane tends to prevent the spreading of the other two methyls, we should expect a larger angle in propane. In cyclohexane there is an additional force operating between opposite carbons in the ring, and although this interaction changes more slowly as the bond angles are varied, it should nevertheless have some effect in tending to flatten the ring. In pyrane, the shorter C−O distances replacing two former C−C distances tend to flatten at least part of the ring, although the oxygen, with its probably smaller C−O−C angle, might be forced somewhat more out of the plane.[20] Finally, since small changes in the angles of the ring make large changes in the distances between the groups attached to the ring, these groups should have a great effect on the form of the ring—tending to make it more flat for some configurations and less flat for others.

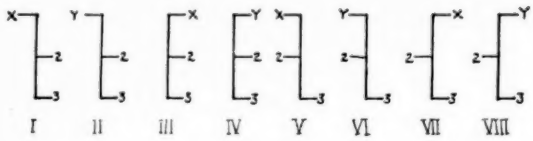


FIG. 4.

Cox[18] has applied x-rays to the study of the dimensions of the unit cells of sugar crystals and from this obtains data indicating a biplanar ring in the solid. We are not sure that his results do not also fit a flattened chair form of the ring.

(b) That the two possible chair forms of a given pyranose sugar (if, indeed, the sugars occur as chair forms) occur in equal amounts seems highly improbable if the C−C−C angle is nearly tetrahedral. Thus, a calculation of the energies arising from quantum mechanical repulsions between groups results in relative energies as shown in Table VII. (These values were obtained by calculating exchange repulsions from Morse curves by the method of Eyring.[21] Other than to show that the two ring forms would be expected to have very much different stabilities, these values have no exact significance,

[17] See reference 6.
[18] E. G. Cox *et al.*, J. Chem. Soc. 1497 (1935). See also reference 7.
[19] J. Y. Beach and D. P. Stevenson, J. Am. Chem. Soc. **60**, 475 (1938).
[20] Reference 18, p. 1497.
[21] H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

since the oxygen-oxygen repulsions used are unreliable.)

As the ring becomes more and more flat, these differences in stability become less marked, since fewer groups interact effectively and differences in distance are smaller. Therefore, it seems reasonable that the rings exist as flattened chairs of which both possible forms occur in about equal amounts. On the other hand, if pyranose rings are biplanar, the present proof of Hudson's rules would require the presence of about equal amounts of both of these possible forms. This seems less likely, but not impossible.

Since the values of $2A$ for the furanoses, which almost certainly have planar rings, are very close to those for the pyranoses, we must recognize a close similarity between the two.

(2) In considering the second condition, we will recognize three kinds of interactions between groups as operative in altering the optical rotations of the sugars:

(a) Vicinal interactions which give rise directly to optical activity.

(b) Interactions which tend to orient the hydroxyl group and other groups about the C−O bond. (These will have considerable effect on the optical activity according to the one-electron theory; Kuhn,[22] too, recognizes this effect as of importance. Kirkwood,[23] however, has not considered this hydroxyl orientation to be significant in his calculation of the optical rotation of *sec*-butyl alcohol, but he does not exclude the possibility that it may actually be of some importance.)

(c) Interactions which tend to force groups out of their required positions relative to the effective plane of symmetry of the ring. These would include those forces which tend to make one form of the ring more stable than another.

These interactions must be additive.

(a) That strictly optical vicinal effects are additive follows as an approximation from many theories of optical activity. Since this is not entirely obvious for the one-electron model, we supply the following proof:

$$[\alpha]_D = K \cdot Im(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a),^{24}$$

$$\psi_a = \varphi_1^0 + \sum a_i \varphi_i^0, \quad a_i = H_{1i}/E_1^0 - E_i^0,$$

$$\psi_b = \varphi_2^0 + \sum b_i \varphi_i^0, \quad b_i = H_{2i}/E_2^0 - E_i^0,$$

where φ_k^0 is the eigenfunction of the chromophoric group in its kth state (unperturbed); H_{ki} is the matrix element of the perturbing field; ψ_n is the perturbed eigenfunction of the chromophoric group in its nth state.

The H_{ki} are made up of the sums of the perturbing effects of the surrounding groups:

$$H_{ki} = \sum_j H_{ki}^{(j)},$$

where $H_{ki}^{(j)}$ is the effect of the jth group, taken alone, on the chromophore under consideration. Therefore:

$$b_i = \sum_j \frac{1}{E_2^0 - E_i^0} H_{2i}^{(j)}, \quad a_i = \sum_j \frac{1}{E_2^0 - E_i^0} H_{1i}^{(j)},$$

$$(a|\mathbf{p}|b) = \mathbf{p}_{12} + \sum_i a_i \mathbf{p}_{i2} + \sum_i b_i \mathbf{p}_{1i},$$

$$(b|\mathbf{m}|a) = \mathbf{m}_{21} + \sum_i a_i \mathbf{m}_{2i} + \sum_i b_i \mathbf{m}_{i1},$$

$$(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a) = \mathbf{p}_{12}\cdot\mathbf{m}_{21} + \sum_i a_i(\mathbf{p}_{i2}\cdot\mathbf{m}_{21} + \mathbf{p}_{12}\cdot\mathbf{m}_{2i}) + \sum_i b_i(\mathbf{p}_{12}\cdot\mathbf{m}_{21} + \mathbf{p}_{1i}\cdot\mathbf{m}_{21}),$$

where terms in $a_i a_k$, $b_i b_k$, etc., are neglected, since they have been found to be small in the sugars. (They may not, however, be small in

TABLE VII. *Relative stabilities of chair forms.*

	α		β	
	CHAIR No. 1	CHAIR No. 2	CHAIR No. 1	CHAIR No. 2
Arabinose	2.23 kcal.	0 kcal.	1.36 kcal.	1.38 kcal.
Xylose	1.13	0	.08	.65
Lyxose	1.02	.19	0	.48
Ribose	0	1.65	1.20	.94

[22] W. Kuhn, Zeits. f. physik. Chemie **B31**, 40 (1935).
[23] J. G. Kirkwood, J. Chem. Phys. **5**, 489 (1937).

[24] (a) L. Rosenfeld, Zeits. f. Physik **52**, 161 (1928). (b) See also, E. Condon, Rev. Mod. Phys. **9**, 441 (1937). This relation corresponds to the contribution of a single transition to the optical rotation. Where several transitions are important we may sum over them, so that our result is not affected.

all cases.) Thus,

$$[\alpha]_D = KIm\{\sum_i [b_i(\mathbf{p}_{12}\cdot\mathbf{m}_{i1}+\mathbf{p}_{1i}\cdot\mathbf{m}_{21}) + a_i(\mathbf{p}_{i2}\cdot\mathbf{m}_{21}+\mathbf{p}_{12}\cdot\mathbf{m}_{2i})+\mathbf{p}_{12}\cdot\mathbf{m}_{21}]\}$$

$$= KIm\left\{\sum_{i,j}\left[\frac{H_{1i}^{(j)}}{E_1^0-E_i^0}(\mathbf{p}_{i2}\cdot\mathbf{m}_{21}+\mathbf{p}_{12}\cdot\mathbf{m}_{2i}) + \frac{H_{2i}^{(j)}}{E_2^0-E_i^0}(\mathbf{p}_{12}\cdot\mathbf{m}_{i1}+\mathbf{p}_{1i}\cdot\mathbf{m}_{21})+\mathbf{p}_{12}\cdot\mathbf{m}_{21}\right]\right\}.$$

That is, the optical activity of a given chromophoric electron is the sum of the separate interactions of the groups of the molecule on that electron. The term, $\mathbf{p}_{12}\cdot\mathbf{m}_{21}$, is ordinarily zero, but it is possible that the unperturbed eigenfunctions have no planes or centers of symmetry, so that this will not vanish. The extension to several chromophoric electrons is obvious. So also is the extension to the explicit expression of the quantities A_{ij}, B_{ij} and A_{jj} of our proof of Hudson's rules.

We may note that this concept of additivity of vicinal interactions might form the basis of a workable rule for calculating optical rotations semi-empirically. It would seem that one reason why such a rule has not already been formulated is that too much attention has been devoted to compounds like tartaric acid, of which little is known about the orientations of the groups, let alone the effects of solvents upon their interactions. Only when substances are investigated in which these uncontrollable effects are subordinated, or in which they may be suitably dealt with in some way, may we expect to get at the beginnings of any kind of workable, general theory of optical rotatory power. Therefore, a study is being made of simple, rigid compounds like methyl cyclopentanone and camphor, of which there is a surprising number in the terpenes, sterols, and alkaloids.

(b) Interactions which tend to orient hydroxyls, etc., will certainly not be additive. If Hudson's rule is to have any simple significance, this forces us to conclude that either: (1) the orientation of a hydroxyl group about its C−O bond has no effect on the partial rotation of the hydroxyl, which in the light of our calculations as well as of Kuhn's work is to be considered as very unlikely. (2) The association of solvent about a hydroxyl reduces these interactions to nil, so that the hydroxyl hydrogens orient at random or so that they take up a position which, though definite, is independent of that of the neighboring groups, or (3) what amounts to Freudenberg and Kuhn's[25] treatment of Hudson's rules if vicinal actions drop off so rapidly with distance that the groups about the carbon atom of the ring twice removed from the glucosidic hydroxyl have no effect on the partial rotation of the glucosidic hydroxyl, then Hudson's rules as well as the outstanding exceptions to them follow immediately, regardless of the planarity of the ring. Since, however, vicinal actions seem to act over longer distances than this view would require (one need only note the large rotation of 3-methyl cyclopentanone); and since the methyl mannofuranosides do not seem to deviate markedly from Hudson's rule[26] (which indicates in general that orientation about the C−O bond will not account for discrepancies in Hudson's rule); and since, finally, octaacetyl neo-lactose (a derivative of galacto-sido-altrose) does obey Hudson's rule (the orientation of the epimeric group in altrose being the same as that in mannose so that by the reasoning of Kuhn and Freudenberg this sugar should not obey Hudson's rules), then, from these three facts, we hold that this view must be inadequate.

The process of elimination leads us to assign the greatest probability to alternative No. 2 as the factor operative here.

(c) Interactions which tend to force groups out of positions of symmetry are certainly not additive in their effect on optical activity. Note that they would not be expected to be operative to any appreciable extent in furanose rings, which are flat and probably not liable to much distortion in the present sense.

It is to the results of the forces of (c) that we ascribe the observed discrepancies in Hudson's rules.

The closer examination of these forces in the light of the above must await a study of their effects on other properties of the sugars. Such a study is now being carried out, but we may

[25] K. Freudenberg and W. Kuhn, Ber. **64**, 719 (1931).
[26] E. Pacsu and A. Scattergood, J. Am Chem. Soc. **61**, 534 (1939).

mention the following as a tentative picture of how they operate. The forces apparently have something to do with the bunching of groups (including CH_2OH groups) on one side of the ring; this may be expected to be a significant factor in modifying the ring form in a direction away from that required by our present proof. Furthermore, this bunching must occur in the neighborhood of the glucosidic carbon and not about the other parts of the ring, in order that it cause a deviation from Hudson's rules. Thus, we expect that altrose and idose will ultimately be found to obey Hudson's rules, while ribose will not; we are, however, uncertain about the behavior of allose.

Since there is more bunching of groups in β-mannose than in α-mannose, β-mannose should be expected to be the more anomalous. This is in agreement with the conclusions of Hudson,[27] who, recognizing the anomaly in β-mannose, sought to explain it by giving it a furanose ring. We see that by the present reasoning, such a drastic step is unnecessary.

Finally, it is clear that there must be no expectation that Hudson's rules should hold with great precision in all solvents or under all other conditions; it is difficult to see how, under all possible circumstances, the various requirements of our proof would always be rigidly obeyed. Therefore, deviations of some sort must at times be looked for, and indeed, it seems quite likely that such deviations will lead to further information about sugar structure and solvent action in general.

E. Two cases requiring special mention

(1) The results of Isbell[15] (that the partial rotation of a hydroxyl in a sugar depends on the orientations of neighboring groups) are in partial contradiction to our conclusions. We account for them on the basis that he has subtracted, in some cases, substances with different average ring conformations. The agreement which he obtains for R_4 is doubtless due to the cancellation of effects similar to that which makes the modified Hudson's rule valid.

(2) Optical superposition in the lactones.[28] The γ-lactones of the pentose sugars should show superposition since they would seem to obey the conditions set forth above. It is found that they do not, and we might attribute this tentatively to a deviation of the lactones from the principle of additivity of optical interactions.

We wish to express our gratitude to Professors Henry Eyring and Eugene Pacsu for helpful discussions relating to the above.

Addendum

We will consider in more detail than in (1) and (2) the relation between the one-electron theory and the polarizability theory of Kirkwood.[29] The Hamiltonian operator for any molecular system can be written symbolically as

$$H=\sum_{i=1}^{n} T_i+\sum_{i=1}^{n} V_i+\sum_{i<j}^{n} V_{ij},$$

where n is the number of electrons, T_i is the kinetic energy operator for the ith electron, V_i is the potential energy of the ith electron in the field of the nuclear network, V_{ij} is the potential energy operator corresponding to the mutual interaction of the ith and jth electrons. The last term is not tractable and can only be handled by approximate methods. Kirkwood breaks the Hamiltonian up into the sum of the Hamiltonians of the substituent groups and then, using an approximate expression for the interaction terms between groups, solves for the eigenfunctions by a perturbation method using the solutions for the individual groups as the zero-order functions. He shows that the rotatory parameter β (which is g in his and Born's[30] notation) can be broken up by a transformation into the sum, $\beta=\beta^{(0)}+\beta^{(1)}+\Sigma\beta^{(k)}$.

On the other hand, in the one-electron theory we replace the interaction terms V_{ij} by an average potential field φ_i representing the interactions of all the other electrons on the ith electron. The approximate Hamiltonian operator then becomes

$$H=\sum_{i=1}^{n} T_i+\sum_{i=1}^{n} V_i+\sum_{i=1}^{n} \varphi_i$$

and the solutions are the products of the one-electron wave functions ψ_n^i. Thus in the normal state we obtain

$$\Psi_0=\prod_{i=1}^{n} \psi_0^i.$$

The ψ_0^i are the solutions of the Hartree equations

$$H_i\psi_0^i=(T_i+V_i+\varphi_i)\psi_0^i=E_0^i\psi_0^i.$$

We consider that only those transitions are important which involve a change in the quantum numbers for only one electron at a time, since simultaneous transitions of more than one electron lie very far out in the ultraviolet and consequently do not contribute appreciably to the optical activity in the visible. It is assumed further that

[27] C. S. Hudson, J. Am. Chem. Soc. **48**, 1424 (1926).
[28] Reference 25, p. 716.
[29] Reference 23, p. 479. We will, also, discuss this subject further at a later date.
[30] M. Born, Physik. Zeits. **16**, 251 (1915).

the fields φ_i are the same for the system with one excited electron as for the normal state. The validity of this assumption was discussed in detail in (1). We may then calculate the optical activity for transitions to such excited states as

$$\Psi_{nk}=\prod_{i\neq n}\psi_k{}^n\psi_0{}^i$$

using Rosenfeld's formula.[24a] $\psi_k{}^n$ refers to the kth excited state of the nth electron. Because of the orthogonality between the functions $\psi_m{}^n$ and $\psi_l{}^n$ $(m\neq l)$,

$$\beta=\frac{c}{3\pi h}\sum_n\sum_k\frac{(\psi_0{}^n|\mathbf{p}|\psi_k{}^n)\cdot(\psi_k{}^n|\mathbf{m}|\psi_0{}^n)}{\nu_{nk}{}^2-\nu^2}.$$

Upon antisymmetrizing the functions, this formula would also be nearly valid since the functions $\psi_k{}^n$ and $\psi_l{}^m$ are nearly orthogonal for $n\neq m$. At any rate, if we used the orthogonalized $\psi_k{}^n$'s, the formula would be exact.

This is analogous to Kirkwood's term $\Sigma\beta^{(k)}$, while on this model terms like his $\beta^{(0)}$ and $\beta^{(1)}$ do not appear.

In order to compare the two theories more fully it is necessary to go back to a consideration of the exact Hamiltonian, and further, to make the comparison more explicit, we can identify the solutions $\psi_n{}^i$ with those of the individual groups in the Hartree fields of the other groups. We can then calculate the solutions for the exact Hamiltonian by a perturbation method as Kirkwood does but using as the perturbation the term $\sum_{i<j}V_{ij}-\sum_i\varphi_i$ instead of simply V_{ij}. The terms in $\beta^{(0)}$ will now appear, but this time as a result of the smaller perturbation $\sum_{i<j}V_{ij}-\sum_i\varphi_i$ instead of V_{ij}, which was used by Kirkwood. We thus see that by our method we have already included a part of the $\beta^{(0)}$'s in our calculations. We might expect that since the perturbation $\sum_{i<j}V_{ij}-\sum_i\varphi_i$ is small, as shown by the fact that Hartree's method usually gives a good approximation to the energy, then its contribution to the optical activity would be small. It would be impossible, however, to make any definite statements as to the magnitude of this effect as far as the optical activity is concerned until explicit calculations are made. It was not deemed feasible to attempt such a calculation since due to the difficulties inherent in the problem both Kirkwood and ourselves were forced to use approximate expressions for the terms V_{ij} and φ_i. We see at any rate that the two points of view are by no means mutually exclusive, and that the one-electron theory and Kirkwood's polarizability theory should profitably supplement one another in future researches on optical activity.

It should be emphasized that because of unavoidable approximations, exact agreement with experiment is not to be expected of our calculations. What can be expected is that the orders of magnitude of the rotations and the relative configurations of the compounds investigated should agree with those observed experimentally—as is the case for the substances here considered.

Intensities of Electronic Transitions in Molecular Spectra

IV. Cyclic Dienes and Hyperconjugation

ROBERT S. MULLIKEN
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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The spectra of cyclopentadiene, 1,3-cyclohexadiene, thiophene, furan, and pyrrole are considered. Theoretical explanations of their departures from the spectra of open-chain conjugated dienes are given. The cause of these departures in the cases of cyclopentadiene and cyclohexadiene is designated hyperconjugation. This is a mild sort of conjugation, apparently not recognized as such hitherto, between saturated groups and double or triple bonds or even other saturated groups. Observed displacements of spectra toward longer wave-lengths, and corresponding effects in the refractivities (cf. VI), when alkyl groups are substituted for hydrogens in ethylene, butadiene, benzene, or other double-bonded compounds, are attributed to hyperconjugation. Further, the decreasing heat of hydrogenation observed with increasing alkyl substitution in these compounds may indicate increasing stability caused by hyperconjugation. However, it is likely according to the theory that appreciable energy effects caused by hyperconjugation are usually restricted to excited states, and so should affect mainly ultraviolet spectra and refractivities. If this is correct, heats of hydrogenation ought not to be much influenced by hyperconjugation, since they depend on the energies of molecules in their normal states. Hence, it is likely that the above-noted variations in heats of hydrogenation are caused partly or mainly by other causes. Conjugation of triple bonds is briefly discussed, and it is also pointed out that in ethane there must be hyperconjugation which is analogous to the triple-bond conjugation in cyanogen. It is shown that this hyperconjugation in ethane should not appreciably hinder free rotation. Likewise, hyperconjugation in propylene should produce no barrier to free rotation of the methyl group. It is possible, however, that hyperconjugation may help to restrict free rotation in some cases. Carbon to carbon single bond distances should be slightly shortened by hyperconjugation. The unusually small C−C distance in methylacetylene as determined spectroscopically by Herzberg and co-workers may perhaps be explained in this way, although in other cases no appreciable effects are apparent. It is helpful to classify examples of hyperconjugation according to various types, which may differ in the magnitudes of their effects. Possibly only first-order hyperconjugation (between a double or triple bond and a saturated group) is important. Second-order hyperconjugation (between two saturated groups, as, for example, in ethane) very likely produces smaller effects.

1. PENTACYCLIC DIENES

ALL conjugated dienes might be considered as derivatives of the simplest known conjugated diene, that is, of 1,3-butadiene. For butadiene, two geometrical forms are conceivable (*cis* and *trans*, cf. Fig. 1 of III of this series[1]). Some derivatives might conceivably have the cis-, others the trans-form. As was shown in III, the long wave-length spectra of all *cis* derivatives of butadiene should be similar, and likewise for all *trans* derivatives. The *cis* and *trans* spectra should be nearly alike as regards frequencies but should differ radically as regards intensity distribution. In the case of noncyclic conjugated dienes, available data were shown to indicate that the molecules of open-chain dienes are wholly or predominantly in the trans-form.

Cyclic conjugated dienes necessarily belong to the *cis* class. It was noted, however, in III that the first absorption region is at considerably longer wave-lengths in cyclopentadiene and cyclohexadiene than in open-chain dienes, and that it seems to be somewhat weaker than expected. It appeared, then, that cyclic dienes require a special treatment. This will now be given. At the same time, we may also consider the molecules pyrrole, furan and thiophene (C_4H_4NH, C_4H_4O, C_4H_4S), and the ion $C_5H_5^-$ ($C_4H_4CH^-$). All of these are closely related to cyclopentadiene ($C_4H_4CH_2$), and all may be considered as cyclic conjugated dienes. In this connection, reference may be made to a paper by Hückel, who has briefly discussed the structures of all these molecules.[2]

[1] R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939): Paper III of this series. For explanation of what is meant by "semi-theoretical *f* values," see footnote 2 of that paper.

[2] E. Hückel, Zeits. f. Physik **70**, 257–60 (1931); Zeits. f. Elektrochem. **43**, 779, 786, 845 (1937). In his 1937 review, Hückel speaks of electrons of the first and second kinds in double bonds. This is good, but the new term "unsaturation electrons" introduced here is chemically descriptive, and less cumbersome than "electrons of the second kind."

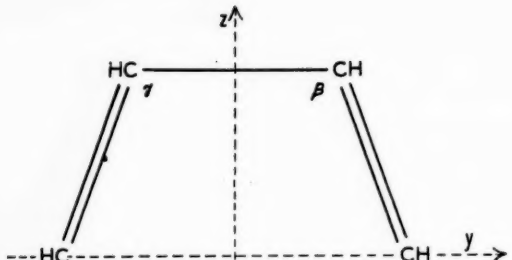


FIG. 1. Cyclic dienes.

Let us label the several atoms, and choose axes y and z, as in Fig. 1. Atoms α, β, γ, δ, constitute a conjugated diene skeleton exactly like that in cisbutadiene (cf. Fig. 1*a* of III). In Fig. 1, A stands for CH_2, CH^-, NH, O, or S. Except when A is CH_2, all atoms in the figure lie in one plane. When A is CH_2 the two hydrogens lie symmetrically in the xz plane, one above and one below the plane of the ring, with an HCH angle presumably near the tetrahedral angle. The symmetry of the complete system in all cases is the same (C_{2v}) as in cisbutadiene.

In predicting the long wave-length spectra of the noncyclic conjugated dienes in III, we considered only the four double-bond "mobile" electrons or "unsaturation" electrons and their four MO's (molecular orbitals) χ_1, χ_2, χ_3, χ_4, (cf. III, Eq. (1) and Table II). This was because these orbitals are the most loosely bound orbitals spectroscopically (cf. III, Section 1), and because they differ from all others in having a node in the plane of the double bonds and so form a distinct species, whose members do not interact with orbitals associated with other bonds in the molecule.

[*Hereafter we shall call orbitals of this species "unsaturation" orbitals, dropping the term "mobile-electron" orbitals* (used in III of this series), to which objections may be raised.[2] Similarly, we shall speak of unsaturation electrons. The same designation can also be applied to the characteristic triple bond π orbitals.]

In the cyclic dienes represented by Fig. 1, however, the atom or radical A in every case contains one pair of electrons in an orbital which is like those of the unsaturation electrons in being antisymmetrical to the plane of the ring. Hence there is interaction between this and the unsaturation orbitals, resulting in what may be called "cyclic conjugation." This phenomenon has been recognized and discussed by Hückel,[2] except for the case where A is CH_2. For this case we may introduce the term "hyperconjugation,"[3] meaning an additional conjugation beyond that ordinarily recognized.

Cyclic conjugation should cause stabilization of the molecular structure in pyrrole, furan and thiophene, and perhaps especially in the $C_5H_5^-$ ion, where there is complete equivalence of the five CH groups and so a particularly intense form of conjugation (let us say "homocyclic conjugation"), like that in benzene. Hyperconjugation, ordinary conjugation, and homocyclic and heterocyclic conjugation are forms of mesomerism or resonance.

The electrons which give rise to heterocyclic conjugation when A is NH, O, or S are a pair which in the absence of conjugation would be nonbonding $2p_z$ electrons.[2] Also when A is CH_2 there is a corresponding pair of electrons, which are capable of giving rise to hyperconjugation. But since these hyperconjugating electrons in cyclopentadiene are already C—H bonding electrons, it is not to be expected that they can contribute nearly as much toward stabilizing the molecule as the, previously nonbonding, cyclically-conjugating electrons in pyrrole, furan and thiophene.

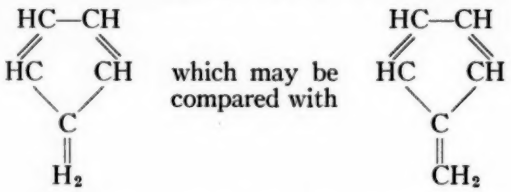
Nevertheless, according to data of Kistiakowsky and co-workers,[4] the heat of hydrogenation is only 50.87 kcal. for cyclopentadiene, as compared with 57.08 kcal. for butadiene. These data suggest an added effect of hyperconjugation in stabilizing cyclopentadiene (6.2 kcal.) which is comparable with the effect of ordinary diene conjugation (6.7 kcal. if we compare, for example, the heat of hydrogenation of 1,3-pentadiene with that of 1,4-pentadiene).

[3] The term "hyperconjugation" was suggested by Professor W. G. Brown, as an improvement on the term "superconjugation" at first used by the writer.

[4] Cf. J. B. Conant and G. B. Kistiakowsky, Chem. Rev. **20**, 181 (1937).

However, it seems possible that the low heat of hydrogenation of cyclopentadiene may be due as much to instability of the aliphatic five-ring as to stability of cyclopentadiene. As possible evidence, the heat of hydrogenation of 1,3-cyclohexadiene (55.37 kcal.) might be cited.[4] Assuming the resulting aliphatic six-ring (cyclohexane) to have normal stability, it appears that hyperconjugation in cyclohexadiene has an appreciable stabilizing effect, but much smaller than the data suggest for cyclopentadiene. Presumably the stabilizing effect of cyclic conjugation in pyrrole, furan and thiophene is in any case much greater than that of hyperconjugation in cyclopentadiene. This is borne out by the low observed value (36.6 kcal.) of the heat of hydrogenation of furan.[4] (See also the discussion at the end of Sections 4 and 6, which indicates that stabilization by hyperconjugation is only a second-order effect in the normal states of cyclopentadiene and cyclohexadiene, and should be a first-order effect in these molecules only in excited states.)

In order to make clearer the nature of hyperconjugation in cyclopentadiene, one may formulate the molecule as having a bond structure



in the fulvene molecule.[5] The essential point, which stands out clearly when one uses the MO method but which is not obvious when one uses the AO method, is that the two H atoms in the CH_2 group in cyclopentadiene should for certain purposes be treated as a unit. Thus the bonding between the ϵ carbon atom in Fig. 1 and this H_2 group has a considerable similarity to a double bond.

This quasi-double bond, like the $C=CH_2$ ordinary double bond in fulvene, contains one pair of electrons which can enter into conjugation with the two pairs of unsaturation electrons belonging to the two double bonds in the ring (for details, cf. Sections 2 and 4). The conjugation is of course not nearly so intense as in fulvene, because the $C=H_2$ quasi-double bond does not enter into as full resonance as if it were just like the others. Molecules intermediate between cyclopentadiene and fulvene (but probably nearer fulvene) in this respect would be those with $C=O$ or $C=NH$ as A in Fig. 1.

Although the MO method shows particularly clearly the quasi-double bond character of the $C=H_2$ bonds, the problem can also be treated by a slight modification of the usual AO method. According to this, we start with a $2p_x$ AO (unsaturation AO) on each carbon atom in cyclopentadiene, and in addition an orbital, belonging jointly to the two H atoms of the CH_2 group, which is easily seen to have a form very similar to that of $2p_x$ of a carbon atom. This H_2 quasi-unsaturation orbital is constructed by taking a subtractive linear combination $(1s_A - 1s_B)/2^{\frac{1}{2}}$ of the ordinary $1s$ AO's of the two hydrogen atoms A and B (cf. Eqs. (2) and (3) in Section 4, and reference 7). We thus have five carbon unsaturation AO's and one similar H_2-group orbital, among which electron pair bonds can be constructed corresponding to various canonical structures, following the usual electron pair AO resonance theory. In the following, however, we shall use exclusively the MO method, in LCAO approximation.

2. Unsaturation Molecular Orbitals for Pentacyclic Dienes

Our first problem is to determine the forms of the unsaturation MO's which arise through interaction of the four butadiene unsaturation AO's or MO's with the conjugating A orbital or orbitals. Since it is not feasible at present to treat the problem quantitatively, it will be helpful to consider certain simple limiting cases between which the true solutions may be more or less bracketed.

As "case I" we may take the case of *simple conjugation* (no cyclic conjugation or hyperconjugation); here the MO's χ_1, χ_2, χ_3, χ_4 are exactly the same as in butadiene, and in addition there is an AO or MO χ_0 belonging to A. In cyclopentadiene a further, excited, CH_2 MO χ_5 is important, and in thiophene two excited sulfur AO's χ_5 and χ_6 need to be considered.

As "case II" we may take the case of *homocyclic conjugation*, with complete equivalence among

[5] The analogy to fulvene was suggested by Professor W. G. Brown.

all the five ring-atom unsaturation AO's, as given by Hückel. This case should be actually realized in $C_5H_5^-$. In pyrrole and furan, the actuality should presumably be somewhat between cases I and II, but with more or less tendency toward case III.

In "case III" we assume simple conjugation modified by *localized perturbations* between χ_0 and χ_1, and (if A is CH_2 or S) between χ_3 and χ_5. The actuality for cyclopentadiene perhaps most nearly resembles this case. Or perhaps we might better have considered a "case IV" with the five ring atoms and the H_2 group taken as equivalent (cf. last paragraphs of Section 1). This case would resemble that of fulvene. Thiophene should in some ways be like pyrrole and furan, in others like cyclopentadiene (see below).

TABLE I. *LCAO approximation forms and energies of unsaturation MO's of pentacyclic dienes.*

NAME OF MO[1]	α_i	β_i	γ_i	δ_i	ϵ_i	ϵ_i'	ENERGY PLUS A CONSTANT[6]
Case I: Simple Conjugation[2, 3]							
$\chi_0 b_1$	0	0	0	0	1	0	$-1.618\epsilon - A$
$\chi_1 b_1$	0.37	.60	.60	.37	0	0	-1.618ϵ
$\chi_2 a_2$	0.60	.37	−.37	−.60	0	0	-0.618ϵ
$\chi_3 b_1$	0.60	−.37	−.37	.60	0	0	0.618ϵ
$\chi_4 a_2$	0.37	−.60	.60	−.37	0	0	1.618ϵ
$\chi_5 b_1$	0	0	0	0	0	1	$0.618\epsilon + A'$
Case II: Homocyclic Conjugation[2, 4]							
$\psi_0 b_1$	.45	.45	.45	.45	.45		-2.000ϵ
$\psi_1 b_1$	.20	−.51	−.51	.20	.63		-0.618ϵ
$\psi_2 a_2$	.60	.37	−.37	−.60	0		-0.618ϵ
$\psi_3 b_1$	.51	−.20	−.20	.51	−.63		1.618ϵ
$\psi_4 a_2$	.37	−.60	.60	−.37	0		1.618ϵ
Case III: Simple Conjugation with Localized Perturbations[2, 5]							
$\psi_0 b_1$	$.37l$	$.60l$	$.60l$	$.37l$	k	0	$-1.618\epsilon - A - D$
$\psi_1 b_1$	$-.37k$	$-.60k$	$.60k$	$-.37k$	l	0	$-1.618\epsilon + D$
$\psi_2 a_2$	.60	.37	−.37	−.60	0	0	-0.618ϵ
$\psi_3 b_1$	$.60k'$	$-.37k'$	$-.37k'$	$.60k'$	0	l'	$0.618\epsilon - D'$
$\psi_4 a_2$	.37	−.60	.60	−.37	0	0	1.618ϵ
$\psi_5 b_1$	$-.60l'$	$.37l'$	$.37l'$	$-.60l'$	0	k'	$0.618\epsilon + A' + D'$

[1] For each of the χ_i's or ψ_i's, the orbital species (b_1 or a_2) is given according to the conventional symbolism for symmetry C_{2v} (cf. Table I of reference 1).

[2] For each of the three cases (see text) the values of the coefficients to be inserted in Eq. (1) are given for each of the χ_i's or ψ_i's. Note that χ_5, ψ_5, ϕ_ϵ', and A' exist only for cyclopentadiene and thiophene, not for pyrrole and furan. A' when it exists is positive and larger than A. A is probably positive for cyclopentadiene and especially furan, but negative for pyrrole and thiophene.

[3] The coefficients and energies for χ_1 to χ_4 of case I are taken from reference 1 for butadiene, using Hückel's solution ($v=0.372$, $w=0.601$, cf. footnote 2 of Table II in III of this series).

[4] The coefficients and energies of case II are based on Hückel's equations for a ring structure with homocyclic conjugation (E. Hückel, Zeits. f. Physik **70**, 242, (1931), Eqs. (35), (36) or *ibid.* **76**, 634 (1932), Eqs. (5)). Hückel's pair of complex ψ's χ^{+1}, χ^{-1} has, however, been combined to give the *real* forms ψ_1 and ψ_2 used here; likewise Hückel's χ^{+2} and χ^{-2} to give the present ψ_3 and ψ_4.

[5] Case III is obtained from case I by assuming that χ_0 is lower in energy than χ_1 in case I and that these two interact only with each other; likewise that χ_3 is lower in energy than χ_5 in case I and that *these* two also interact only with each other. We have $k>l$ or $k<l$ according as A is positive or negative (cf. note 2 above). Probably χ_0 is much closer to χ_1 than χ_3 to χ_5, making $D>D'$ and $k>k'$. Strictly speaking, there should be four distinct energy constants instead of the two constants D and D', but the use of two constants should represent a tolerably good approximation. Similarly there should be eight constants instead of just k, l, k', l' (cf. e.g., R. S. Mulliken, J. Chem. Phys. **3**, 578 (1935), in connection with the perturbation problem involved here). Case III is applicable especially to cyclopentadiene.

[6] Note that a common negative constant has been omitted from all the energy values given, and should be restored if one wishes the absolute MO energies or term values. The quantity ϵ here represents the "resonance energy" integral; not to be confused with the coefficients ϵ_i.

The forms of the MO's can all be expressed in LCAO approximation by the following equation:

$$\chi_i \text{ or } \psi_i = \alpha_i\phi_\alpha + \beta_i\phi_\beta + \gamma_i\phi_\gamma + \delta_i\phi_\delta + \epsilon_i\phi_\epsilon + \epsilon_i'\phi_\epsilon'. \quad (1)$$

The coefficients α_i, β_i and so on for the several MO's from χ_0 to χ_4 or χ_5,—or ψ_0 to ψ_4 or ψ_5,—and for the three cases, are given in Table I. The χ symbols will be used in the "unperturbed" case I, the ψ symbols in the "perturbed" cases II and III. The orbitals ϕ_α to ϕ_ϵ in Eq. (1) are simply $2p_x$ orbitals of the five ring atoms α to ϵ (cf. Fig. 1), except that in the case of cyclopentadiene, ϕ_ϵ is more complicated (see Eqs. (2)). The orbital ϕ_ϵ' occurs only for cyclopentadiene (see Eqs. (3)) and for thiophene (see below).

From Table I it will be seen that the MO's χ_2 and χ_4, which are of the orbital species a_2, are unaffected by cyclic conjugation or hyperconjugation (except perhaps in thiophene, see below); that is, ψ_2 and ψ_4 of cases II and III are, respectively, identical with χ_2 and χ_4 of case I. The remaining MO's, all belonging to the species b_1, *are*, however, affected. The orbital species b_1 and a_2 are characterized by the following properties: both are antisymmetrical to the plane of the ring atoms, while a_2 is antisymmetrical but b_1 symmetrical to the xz plane in Fig. 1.

Of most interest to us is the longest wavelength singlet→singlet transition $N \rightarrow V_1$, which corresponds to the MO transition $\psi_2 \rightarrow \psi_3$, analogous to $\chi_2 \rightarrow \chi_3$ in the noncyclic dienes (cf. III, especially Eqs. (2)). Since ψ_2 is unaffected by cyclic conjugation and is identical with χ_2, the frequency and intensity of $N \rightarrow V_1$ should be influenced primarily by the changes in ψ_3 as compared with χ_3.

3. PYRROLE AND FURAN

In pyrrole and furan, the effect of cyclic conjugation on χ_3 (as one sees by comparing

cases I and II of Table I) should be to raise its energy and so to increase the frequency of $N \rightarrow V_1$ as compared with noncyclic dienes. The intensity, however, should be nearly the same as for *cis* derivatives of butadiene with the same θ, as one can show by calculating Q_y in the same way as was done in getting Eq. (7) of III. Assuming $\theta = 20°$, this would mean an f value for $N \rightarrow V_1$ of about 0.08 (cf. Table V of III, multiplying the semi-theoretical f given there[1] by the empirical correction factor $\frac{1}{4}$ as estimated in III). It should be noticed, however, that in pure case II of Table I, the transitions $N \rightarrow V_2$, $N \rightarrow V_3$, and $N \rightarrow V_4$ (involving the respective MO changes $\psi_2 \rightarrow \psi_4$, $\psi_1 \rightarrow \psi_3$, and $\psi_1 \rightarrow \psi_4$) would all have the same frequency as $N \rightarrow V_1$; the total intensity of all four transitions would correspond to a total f value of perhaps about 0.3, with a frequency about the same as for $N \rightarrow V_2$ and $N \rightarrow V_3$ in butadiene (about 58,500 cm^{-1} according to III, Table V).

The incomplete experimental data[6] on pyrrole and furan in hexane solution (cf. Table II) seem to be in general agreement with the pure case II prediction, except that it looks as if the absorption maxima come near 50,000 cm^{-1} rather than 58,500 cm^{-1}. The actual positions of the maxima are rather uncertain, since they come below the limits of observation, which were at 46–48,000 cm^{-1}.

Consideration of appearance-pressure data on pyrrole vapor, however (cf. Table II), indicates a rather different state of affairs. According to Scheibe and Grieneisen,[7] pyrrole vapor shows fairly strong absorption from about 45,000 cm^{-1} down to at least 62,000 cm^{-1} (their limit of observation), with major maxima at 47,320, at 54,000, and at 59,000 cm^{-1}. This arrangement agrees rather well with what is predicted for case III of Table I, if we identify the three maxima as $N \rightarrow V_1$, $N \rightarrow V_3$, and $N \rightarrow V_2$, respectively. In case III, $N \rightarrow V_1$ is predicted to come at about the same position (47,000 cm^{-1}) as for open-chain dienes, $N \rightarrow V_3$ at a lower frequency than the value 58,500 cm^{-1} predicted for the latter, and $N \rightarrow V_2$ at the same frequency 58,500 cm^{-1} as for the latter. The relative intensities then also appear consistent with the predictions for case III. (The predictions are easily made by using Table I, case III of the present paper and Table V of Paper III.)

The existence of the maximum of absorption at 47,320 cm^{-1} in pyrrole as found by Scheibe and Grieneisen[7] contradicts the steadily rising form of the absorption curve as found by Menczel[6] in hexane solution. In explanation, it seems possible that Scheibe and Grieneisen's maximum is really a shoulder on a rising absorption curve rather than a true maximum. Such an error seems not unlikely in view of the fact that Scheibe and Grieneisen's curve is based on appearance pressures of absorption regions, using photographs, and not on quantitative measurements. New quantitative measurements for pyrrole and furan, preferably on their vapors, would be of interest.

The thiophene spectrum differs considerably from those of pyrrole and furan, and resembles that of cyclopentadiene (cf. Table IV). This may probably be attributed to the influence of sulphur $3d$ orbitals (cf. Section 4).

4. Cyclopentadiene

Let us now consider cyclopentadiene. If for the moment we treat the CH_2 group of this molecule as if it were isolated,[8] the C–H bonding in terms of MO's is taken care of by four electrons occupying two bonding MO's, say ω_ϵ and ϕ_ϵ, which in LCAO approximation have the following forms:

$$\left.\begin{aligned} \omega_\epsilon &\approx \lambda_1(2p_z + \rho 2s) + \mu_1(1s_A + 1s_B) \\ \phi_\epsilon &\approx \lambda_2(2p_x) + \mu_2(1s_A - 1s_B) \end{aligned}\right\}. \qquad (2)$$

Here $1s_A$ and $1s_B$ refer to $1s$ orbitals of the two hydrogen atoms, $2s$, $2p_x$, and $2p_z$ to orbitals of the ϵ carbon atom (A in Fig. 1). Besides ω_ϵ and ϕ_ϵ, the corresponding antibonding orbitals ω_ϵ' and ϕ_ϵ' are of interest:

$$\left.\begin{aligned} \omega_\epsilon' &\approx \lambda_3(1s_A + 1s_B) - \mu_3(2p_z + \rho' 2s), \\ \phi_\epsilon' &\approx \mu_4(2p_x) - \lambda_4(1s_A - 1s_B) \end{aligned}\right\}. \qquad (3)$$

[6] See especially *International Critical Tables*, Vol. V, p. 363, Fig. 20; also *Landolt-Börnstein Tabellen*, 5th Edition, Ergänzungsband II, figure, and Ergänzungsband III, references.

[7] Cyclopentadiene and pyrrole vapor: G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **25B**, 54 (1934); hexane solution, reference 6.

[8] Cf. R. S. Mulliken, Phys. Rev. **41**, 752 (1932); **43**, 297 (1933); J. Chem. Phys. **1**, 500 (1933). J. E. Lennard-Jones, Trans. Faraday Soc. **30**, 70 (1934).

Of the four C−H bonding and antibonding orbitals, two, namely ϕ_ϵ and ϕ_ϵ', are antisymmetrical with respect to the plane of the ring and so can enter into interaction with the unsaturation orbitals. However, since ϕ_ϵ and ϕ_ϵ' belong to the species b_1 (cf. III, Table I), they can interact only with those diene orbitals χ_1 and χ_3 which are of the same species (cf. Table I, case I). In Table I, case I for cyclopentadiene (zero interaction of CH_2 with diene orbitals assumed), ϕ_ϵ and ϕ_ϵ' appear under the names $\chi_0 b_1$ and $\chi_5 b_1$. It is probable that χ_0 and χ_1 of case I are rather close together and interact relatively strongly; likewise χ_5 is probably fairly near (above) χ_3 and may interact rather strongly with it. Strictly speaking, of course, all the four orbitals χ_0, χ_1, χ_3, and χ_5 of case I must interact together, but the "case III" assumption of paired interactions (χ_0, χ_1 and χ_3, χ_5) may represent a reasonably good approximation for cyclopentadiene. One cannot, however, deny the possibility of a considerable tendency toward case II. The relation $k>l$ given in Table I (note 5) for case III is based on the probable supposition that in case I χ_0 is below χ_1; if the reverse should be true, then $k<l$, but this makes no important difference. In any case, $k'>l'$ is fairly certain.

We may then assume case III of Table I, perhaps somewhat modified in the direction of case II, to be applicable to cyclopentadiene. The states N, T_1, V_1 (cf. Eqs. (2) of III) may now be described by:

$$\left.\begin{array}{r} N\colon (\psi_0)^2(\psi_1)^2(\psi_2)^2,\ {}^1A_1 \\ T_1,\ V_1\colon (\psi_0)^2(\psi_1)^2(\psi_2)(\psi_3),\ {}^3,\ {}^1B_2 \end{array}\right\}. \qquad (4)$$

The transition $N\rightarrow V_1$ involves the MO transition $\psi_2\rightarrow\psi_3$. The energy change for this transition, according to Table I, is now $1.218\epsilon - D'$, compared with 1.219ϵ for noncyclic dienes (cf. $\chi_2\rightarrow\chi_3$ in case I of Table I). The observed rather large shift of 4200 cm^{-1} for $N\rightarrow V_1$ in cyclopentadiene vapor[7] as compared with butadiene vapor (cf. Table VI of III) may then be identified with the quantity D'.

It will be noted that no such shift is observed in pyrrole and furan. This difference can be reasonably explained by the fact that χ_5 of case I, which enters here in case III to push down the energy of χ_3 in making the latter into ψ_3, has no analog in pyrrole and furan.

As was mentioned earlier, not only is the frequency of $N\rightarrow V_1$ shifted in cyclopentadiene as compared with open-chain conjugated dienes, but also the intensity is apparently only about half as large as expected in comparison with open-chain dienes of the *cis* type (cf. III, Section 6 and Table VII). A reasonable explanation can be given by using case III of Table I. For the dipole-

TABLE II. *Experimental data on conjugated cyclic dienes.*

SUBSTANCE[1]	STATE	OBSERVER[1]	$\nu_{max}(N\rightarrow V_1)$[2]	$f(N\rightarrow V_1)$[1, 2]	ν_{min}[2]	ν_{max}
Pyrrole	vapor	SG	47,320			54,000; 59,000
	hexane sol.	Me	(49,000)	(0.4?)		
Furan	hexane sol.	Me	(50,000)	(0.5?)		
Thiophene	hexane sol.	Me	42,400	0.05	(51,000)	
Cyclopentadiene	vapor	SG	44,000	—	49–58,000	
	hexane sol.	He	42,000	0.05		
	sol?	Ley	41,700	0.04		
Cyclohexadiene	vapor	St	38,500	0.1? broad	44,400	47,000 (strong)
	cyclohexane sol.	Al	39,100	0.07	45,700	(54,000, $f\approx 0.45$)
α-phellandrene (2-methyl-5-isopropyl-cyclohexadiene)	vapor	St	38,800	weak	41,500	47,600; 53,000 (strong)

[1] Cf. Paper III, Table VI, footnotes 1, 2, 4, 6 for explanation and most of sources. *In addition, note*: Me refers to Menczel;[6] on α-phellandrene and cyclohexadiene, cf. J. Stark *et al.*, *Jahrbuch der. Rad. und Elek.*, Vol. 10, (1913), p. 169 and p. 182 footnote 2.
[2] Values in parentheses are estimates depending in part on extrapolation of absorption curves somewhat beyond the limit of observation.

moment Q we now have (cf. Eq. (4) of III)

$$\left.\begin{aligned} Q(N\rightarrow V_1) &= 2^{\frac{1}{2}}\int \psi_2 y \psi_3 dv \\ &= 2^{\frac{1}{2}}k'\int \chi_2 y \chi_3 dv \end{aligned}\right\}, \qquad (5)$$

the second equality being obtained by comparing cases I and III in Table I and noting that $\int \chi_2 y \phi_\epsilon' dv = 0$. According to Eqs. (5), Q^2 should be smaller here than for open-chain dienes, where $Q = 2^{\frac{1}{2}}\int \chi_2 y \chi_3 dv$, by a factor k'^2. The f value of the transition should be less by the same factor, times a further factor slightly less than 1 because of the lowered frequency. Since $k'^2 + l'^2 \approx 1$, and $k' > l'$ (cf. Table 1), k'^2 should lie between $\frac{1}{2}$ and 1. Thus the low intensity of $N\rightarrow V_1$ in cyclopentadiene can be to some extent accounted for.

How is it now with the transitions $N\rightarrow V_2$, and so on, in cyclopentadiene? Consideration of Table I, case III, including the estimated energies, together with estimation of f values by the usual methods (ending by applying the empirical factor 0.25, as in paper III,[1] to the empirical f values), leads to the following approximate predictions: $N\rightarrow V_3(\psi_1\rightarrow\psi_3)$ should be shifted toward longer wave-lengths by $D+D'$, and so should fall at about 50,000 cm^{-1}, with an f value of perhaps about 0.05. $N\rightarrow V_2(\psi_2\rightarrow\psi_4)$ should come in its normal position and have normal f (58,500 cm^{-1} with $f=0.11$ according to Table V of Paper III after multiplying by 0.25). Beyond this, besides $N\rightarrow V_4$, there should be a number of new $N\rightarrow V$ transitions, corresponding to $\psi_2\rightarrow\psi_5$, $\psi_1\rightarrow\psi_5$, $\psi_0\rightarrow\psi_3$, $\psi_0\rightarrow\psi_4$, $\psi_0\rightarrow\psi_5$, and to $\psi_0\rightarrow\omega_\epsilon'$, $\psi_1\rightarrow\omega_\epsilon'$, $\omega_\epsilon\rightarrow\psi_3$, $\omega_\epsilon\rightarrow\psi_5$, and $\omega_\epsilon\rightarrow\omega_\epsilon'$ (cf. Eqs. (2), (3) for ω_ϵ and ω_ϵ'). However, these transitions should fall at and beyond about 60,000 cm^{-1}. They should contain a considerable part of the unsaturation-electron $N\rightarrow V$ absorption intensity of cyclopentadiene, plus nearly all of the $N\rightarrow V$ intensity associated with the CH_2 group; a small fraction of the CH_2 $N\rightarrow V$ absorption is mixed into the $N\rightarrow V_3$ absorption. [Actually, matters are somewhat more complicated in that there are interactions between ω_ϵ, ω_ϵ' and orbitals associated with all the C–C and C–H bonds in the plane of the molecule. Hence the $N\rightarrow V$ spectrum of the CH_2 group is not sharply separable from the $N\rightarrow V$ spectra of the various other C–C and C–H bonds. But all this should come beyond about 60,000 cm^{-1}.]

Summarizing, a rather weak or moderate absorption is predicted for the region 48,000–56,000 cm^{-1}, followed by increasing absorption becoming strong near or beyond 60,000 cm^{-1}. The cyclopentadiene vapor spectrum as observed by Scheibe and Grieneisen[7] shows a narrow region of moderate absorption with sharp peaks (total f possibly 0.03(?) by comparison with $N\rightarrow V_1$) from 50,000–52,000 cm^{-1}, then rather weak absorption to nearly 60,000 cm^{-1}, followed by a sharp rise and strong absorption thereafter. In a rough way this agrees with the predictions. The major prediction that most of the intensity is beyond 60,000 cm^{-1} is certainly confirmed. The narrow region 50,000–52,000 looks like a Rydberg series transition; if it is so, it should be left out of our considerations. The total f value for the region 50,000–60,000 is in any case small. As will be seen in Paper VI, the absence of strong absorption at wave numbers smaller than 60,000 cm^{-1} is in accord with the experimental data on molecular refractivity.

Let us consider now the energy of the normal state of cyclopentadiene. The energy change due to hyperconjugation should be obtained by comparing the total energy of six electrons (cf. Eqs. (4)) occupying the three orbitals ψ_0, ψ_1, and ψ_2 (case III) with that of six electrons occupying the orbitals χ_0, χ_1, and χ_2 (case I). Referring to the energy information given in the last column of Table I, it is found that in the approximation there used, the energy change should be zero. The same is true for the excited state V_3, but for V_1, V_2 and V_4, there are energy changes $-D'$, $-D-D'$, and $-D$, respectively. Hence, to the approximation used, the energy changes (decreases) due to hyperconjugation are confined to certain excited states. By using a better approximation, we should, of course, find that hyperconjugation changes (most likely decreases) the energy of the normal state. The change is probably considerably smaller than for the excited states, since it is found only in a higher order of approximation. [It may be noted that in the case II approximation the energy of the normal state would be *increased*. While such a result is not entirely unreasonable, it should be recalled that case II is based on somewhat different simplifying assumptions than cases I and III (cf. III, Table II and references given there).]

5. Thiophene

According to available data,[6] thiophene in hexane solution shows its first strong absorption peak (presumably $N \rightarrow V_1$) at about $\nu = 42{,}400$ cm^{-1}, nearly the same as for cyclopentadiene (cf. Table II). The f value is about the same as for cyclopentadiene, although the shape of the absorption curve is considerably different. Beyond the peak, the absorption falls to 50,000 cm^{-1} at least. Thus the thiophene spectrum to $\lambda 2000$ resembles that of cyclopentadiene more closely than those of pyrrole and furan.

In cyclopentadiene, as we have seen, the decisive element in pushing $N \rightarrow V_1$ to longer wave-lengths is the interaction of the C–H-antibonding excited orbital ϕ_ϵ' on χ_3, which pushes down the energy of the latter while converting it into ψ_3 of case III. In pyrrole and furan, on the other hand, there is no excited orbital analogous to ϕ_ϵ'. At first one might suppose that thiophene would be very similar to pyrrole and furan in this respect.

A new element of possible significance, however, is the fact that the $3d$ excited orbitals are relatively lower in energy for the S than for the O atom. [Nevertheless, $4s$ and $4p$ are lower than $3d$ even for sulfur.] Of the five $3d$ orbitals as quantized in the field of force of the thiophene ring (C_{2v} symmetry), *one* is of the species b_1 and so is capable of functioning like ϕ_ϵ' of cyclopentadiene in pushing χ_3 down. Of special interest is the fact that the form of this $3db_1$ orbital, which has the xy and yz planes as nodal planes (taking axes through the S atom), is well adapted to interact strongly with χ_3. In this the $4pb_1$ (i.e., $4p_x$) orbital can also help. The joint action of $3bd_1$ and $4pb_1$ on χ_3 in thiophene may well be as effective as the action of ϕ_ϵ' on χ_3 in cyclopentadiene, and be similarly adequate to explain the observed spectrum.[9] This applies both to the frequency and to the intensity of $N \rightarrow V_1$.

[9] If we suppose that $3db_1$ is active in depressing $\chi_3 b_1$ in thiophene, we ought not to overlook that one of the five $3d$ orbitals is of the species a_2 and so should act to depress $\chi_2 a_2$, which even in cyclopentadiene was not affected according to our previous discussion. But in view of the relatively unfavorable form of $3da_2$, its relatively large energy distance from χ_2, and the absence of help from any $4s$ or $4p$ excited orbitals, it seems safe to dismiss this depression of χ_2 as of minor importance.

6. 1,3-Cyclohexadiene

As will be seen from Table II, cyclohexadiene shows a weak $N \rightarrow V_1$ transition (probably stronger than in cyclopentadiene, however), at surprisingly long wave-lengths ($\nu = 38{,}500$ in the vapor according to Stark, the shift being 9,700 cm^{-1} as compared with butadiene vapor; or 39,100 in solution according to Alsopp, with a shift of 7000 cm^{-1} as compared with butadiene in solution). At $\nu = 47{,}000$ cm^{-1} (or 54,000 cm^{-1}?) there is strong absorption, presumably $N \rightarrow V_3$ but much stronger than $N \rightarrow V_3$ in cyclopentadiene. The higher intensity of $N \rightarrow V_1$ as compared with cyclopentadiene can be accounted for (cf. Table VII of III) by the larger θ, which is estimated to be about 33° here. The relative weakness of $N \rightarrow V_1$ as compared with what is predicted in Table VII of III for $\theta = 33°$ *cis*, and the very large wave-length shift, can be accounted for by hyperconjugation.

In 1,3-cyclohexadiene, we have *two* CH_2 groups and therefore (assuming still a plane ring) *two* CH_2 bonding MO's analogous to ϕ_ϵ and *two* CH_2 antibonding MO's analogous to ϕ_ϵ' of Eqs. (1), (2), (3). Let us imagine the lower part of Fig. 1 expanded to form a six-ring, with *two* A's at the bottom, symmetrically located one on each side of the z axis, and labeled ϵ and η, respectively. Our four CH_2 MO's just mentioned may then be called ϕ_ϵ, ϕ_η, ϕ_ϵ', and ϕ_η'.

If we proceed in the same general way as for cyclopentadiene, starting from the analog of case I of Table I as "unperturbed" case and proceeding to the analog of case III of Table I, we get[10] as final approximate MO's for cyclo-

[10] Eqs. (6) are easily obtained by first drawing an energy level diagram for the unperturbed case, with $\chi_1 b_1$, $\chi_2 a_2$, $\chi_3 b_1$, and $\chi_4 a_2$ at energies $C - 1.618\epsilon$, $C - 0.618\epsilon$, $C + 0.618\epsilon$ and $C + 1.618\epsilon$, respectively (cf. Table I, case I). The MO's ϕ_ϵ and ϕ_η are then assumed to lie just below χ_1, and ϕ_ϵ' and ϕ_η' just above χ_4; but the pair ϕ_ϵ, ϕ_η interact slightly to give two new unperturbed orbitals $a(\phi_\epsilon + \phi_\eta)$ of species b_1 and $b(\phi_\epsilon - \phi_\eta)$ of species a_2, forming a close pair just below χ_1 on the energy diagram. Similarly ϕ_ϵ' and ϕ_η' are replaced by a close pair $c(\phi_\epsilon' + \phi_\eta')$ and $d(\phi_\epsilon' - \phi_\eta')$, respectively, of species b_1 and a_2, lying just above χ_4. Interactions are now assumed between pairs of unperturbed MO's which belong to the same species and are close together on the unperturbed energy level diagram. The results are not materially altered if ϕ_ϵ and ϕ_η should be a little above instead of below χ_1, and so forth. Strictly, the coefficients and energy quantities called k, k', A, and so on should be replaced by a greater variety of symbols, but there is probably no very serious error in the assumed equalities of various coefficients or energy quantities indicated by the parsimonious set of symbols used in Eqs. (6).

hexadiene, and their relative energies E,

$$\left.\begin{aligned}
&\psi_0 b_1 \approx 2^{-\frac{1}{2}}k(\phi_\epsilon+\phi_\eta)+l\chi_1; \\
&\qquad E_0 \approx -1.62\epsilon-A-D \\
&\psi_{00} a_2 \approx 2^{-\frac{1}{2}}k'(\phi_\epsilon-\phi_\eta)-l'\chi_2; \\
&\qquad E_{00} \approx -0.62\epsilon-A'-D' \\
&\psi_1 b_1 \approx k\chi_1-2^{-\frac{1}{2}}l(\phi_\epsilon+\phi_\eta); \quad E_1 \approx -1.62\epsilon+D \\
&\psi_2 a_2 \approx k'\chi_2+2^{-\frac{1}{2}}l'(\phi_\epsilon-\phi_\eta); \; E_2 \approx -0.62\epsilon+D' \\
&\psi_3 b_1 \approx k'\chi_3+2^{-\frac{1}{2}}l'(\phi_\epsilon'+\phi_\eta'); \; E_3 \approx 0.62\epsilon-D' \\
&\psi_4 a_2 \approx k\chi_4-2^{-\frac{1}{2}}l(\phi_\epsilon'-\phi_\eta'); \quad E_4 \approx 1.62\epsilon-D \\
&\psi_5 b_1 \approx 2^{-\frac{1}{2}}k'(\phi_\epsilon'+\phi_\eta')-l'\chi_3; \\
&\qquad E_5 \approx 0.62\epsilon+A'+D' \\
&\psi_6 a_2 \approx 2^{-\frac{1}{2}}k(\phi_\epsilon'-\phi_\eta')+l\chi_4; \\
&\qquad E_6 \approx 1.62\epsilon+A+D.
\end{aligned}\right\} \quad (6)$$

In Eqs. (6), a common negative constant should be added to all the E's to give the absolute MO energies or term values.

The transition $N \rightarrow V_1$ corresponds to $\psi_2 \rightarrow \psi_3$ just as in cyclopentadiene, but the predicted energy change is now $1.24\epsilon-2D'$ as compared with $1.24\epsilon-D'$ for cyclopentadiene and 1.24ϵ for noncyclic dienes. The larger shift is due to the fact that χ_2 interacts with $(\phi_\epsilon-\phi_\eta)$ here, and is pushed up in energy, whereas in cyclopentadiene χ_2 did not interact with ϕ_ϵ for reasons of symmetry. The large shift of 7000 cm^{-1} (or 9700 cm^{-1}?) here observed, as compared with 4200 cm^{-1} for cyclopentadiene, is reasonably accounted for by the foregoing discussion. A similar shift is also observed in α-phellandrene, which is a derivative of 1,3-cyclohexadiene (cf. Table II). That hyperconjugation should lower the $N \rightarrow V_1$ intensity somewhat (although apparently less than observed) in cyclohexadiene can also be shown.

Turning now to the energy of the normal state of cyclohexadiene, remarks similar to those made for cyclopentadiene at the end of Section 4 are applicable. In the case III approximation corresponding to Eqs. (6), the energy changes as compared with case I are as follows for the respective states N, V_1, V_2, V_3, and V_4: zero, $-2D'$, $-D-D'$, $-D-D'$, $-2D$.

7. Hyperconjugation in Other Systems; Conjugation of Triple Bonds; Free Rotation

Whenever methyl or other groups are attached to carbon atoms having unsaturation electrons, there should be hyperconjugation. For instance, two of the six C−H bonding electrons in a CH_3 group attached to a double-bonded carbon atom must be allocated in MO approximation to a quasi-unsaturation MO, i.e., to an MO whose symmetry permits it to interact with the unsaturation MO's.

When two methyl or other groups are substituted for H atoms on one carbon atom in ethylene, the $N \rightarrow V$ spectrum is considerably broadened out and shows a tendency to split into two parts.[11] Further, data of Kistiakowsky and co-workers on heats of hydrogenation of methylated ethylenes[4] tend to indicate an increasing stability of the double bond with increase in the number of substituted methyl groups. It seems worth while to consider whether all these effects may not reasonably be attributed to hyperconjugation between the alkyl groups and the double bond. However, heats of bromination[12] show an opposite trend to that of the heats of hydrogenation, and thus suggest that the heat effects mentioned are due (partly at least) to causes other than hyperconjugation.

The foregoing evidence can very likely be harmonized along the following lines. As we have seen from the theoretical discussion at the ends of Sections 4 and 6, the effects of hyperconjugation are probably very considerably larger for the V excited states of cyclopentadiene and cyclohexadiene than for the normal states N of these molecules. A little consideration of the theory indicates that a similar relation should probably apply to hyperconjugation in general. From the experimental side, also, the most abundant and trustworthy evidence for hyperconjugation comes, on the whole, from ultraviolet spectra and from refractivities (cf. VI), for both of which excited electronic states are important. In the case of properties involving just the normal states (heats of hydrogenation, bond-distances), there are data which are explainable by hyperconjugation, but there is also contradictory evidence. On the whole, it appears that hyperconjugation must have some effect on energies and bond-distances in the normal states

[11] E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 763 (1936): Fig. 2.

[12] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, J. Am. Chem. Soc. **60**, 2764 (1938).

of molecules, but that other influences may be equally or more important in most cases.

The chief effects of hyperconjugation should then usually be on excited states, hence on ultraviolet spectra, refractivities, and polarizabilities. However, normal states may conceivably be relatively strongly affected in special cases. In the following pages we shall consider various features of a number of types of molecules, with a view to seeing what if any connection these properties may have with hyperconjugation. That is, we shall not immediately exclude the possibility that hyperconjugation may sometimes be of appreciable importance for the normal states of molecules.

Returning to the consideration of particular molecules, the alkyl-substituted butadienes, like the alkylated ethylenes, show decreasing heats of hydrogenation with alkylation.[4] Further, the $N \rightarrow V_1$ spectrum shows shifts toward longer wave-lengths when butadiene is alkylated (cf. III, Table VI); these we may reasonably attribute to hyperconjugation. Even the variations which apparently exist in the $N \rightarrow V_1$ f values of different butadiene derivatives (cf. III, Table VI) may be due to hyperconjugation rather than to the *cis-trans* isomerism to which they were tentatively attributed in III. This will be further discussed in VI, Section 6. Similar remarks apply also to unconjugated dienes and (cf. VI, Section 6) to methylated benzenes, styrols and other types.[4]

In II of this series (Section 5, p. 30) it was pointed out that the broadening of the absorption region in methylated ethylenes could be attributed to a reduction in the restoring force constant for torsional vibrations. This would probably carry with it a lowering of the potential hill between *cis* and *trans* isomers. These effects, it is suggested here, may perhaps have hyperconjugation as their basic cause, although a more thorough examination of the problem is needed, in which all the valence electrons shall be considered.

In this connection, attention may be called to an earlier discussion by the writer,[13] in which it was shown that an effect somewhat similar to what is here called hyperconjugation must exist in ethylene when the two CH_2 groups have been twisted through 90° relative to each other (perpendicular C_2H_4). For this configuration, a kind of hyperconjugation must exist between the one "$[x]$" unsaturation electron of each CH_2 group and a pair of quasi-unsaturation electrons "$[y]$" involved in C−H bonding in the other CH_2 group. The unsaturation electrons, which otherwise would be wholly nonbonding in perpendicular C_2H_4, contribute somewhat to the bonding because of this hyperconjugation, and the barrier to free rotation in C_2H_4 must be lowered thereby. It seems likely that further hyperconjugation involving CH_3 or other substituted groups is quantum-mechanically compounded with this effect to cause still further lowering of the *cis-trans* potential hill in substituted ethylenes.

Recently Kistiakowsky and co-workers[14] have suggested that there is a need for a new explanation of the restricting potentials which hinder rotation around single bonds. They conclude, however, that "electron pairs forming double bonds do not take part in this orienting interaction" in cases such as that of the rotation of a CH_3 group in propylene. They also conclude that the potential curve for rotation of CH_3 in propylene has a threefold, not a sixfold, symmetry.

It might seem that these results contradict our conclusion that hyperconjugation, even though small in its energy effects, should exist in the normal states of methyl-substituted ethylenes, since one would suppose off-hand that hyperconjugation would tend to stabilize certain orientations of the methyl group. On looking into the matter, however, it can be shown that there probably should not be any such stabilization. This can be seen by drawing pictorial diagrams of the hyperconjugating MO's of the CH_3 group for various orientations of the latter. If we consider only the four conjugating electrons in the chain $H_3{\equiv}C-C=C$, neglecting the other electrons and leaving out of account the other H atoms, it is easily seen that the energy of the system is unchanged for successive rotations of the CH_3 group by 60° around its axis, and that it is probably little if at all changed for rotations

[13] R. S. Mulliken, Phys. Rev. **43**, 301–2 (1933): Section 8*e*.

[14] G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, J. Chem. Phys. **6**, 900 (1938).

through intermediate angles. (Details of the argument will not be given here; they are rather similar to those given below for ethane.)

But when one considers electrostatic and other effects of the hydrogen atoms neglected in the preceding consideration, it is readily seen that there must be energy variations with a 120° period. Thus the possibility of hyperconjugation seems to be entirely consistent with Kistiakowsky's conclusions on propylene.

Although the problem of free rotation is only incidental to the present paper, it seemed of interest to examine one more example, that of ethane, to see whether hyperconjugation could perhaps help to account for the potentials which hinder free rotation there. We may begin by comparing the following chemical formulas:

$$\mathrm{N{\equiv}C{-}C{\equiv}N},$$
$$\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}H},$$
$$\mathrm{H_3{\equiv}C{-}C{\equiv}H_3}.$$

In cyanogen and diacetylene, there are two conjugated triple bonds; the quantum-mechanical theory of the structure (using either AO's or MO's) is easily seen to be similar to that for two conjugated double bonds as in 1,3-butadiene. Also, one can predict that the longest wavelength electronic spectra of diacetylene and acetylene should differ in much the same way as those of transbutadiene and ethylene.

If we regard each H_3 group as a unit (cf. discussion of the H_2 group in cyclopentadiene, at the end of Section 1), ethane is analogous to cyanogen and diacetylene, and there should be at least a small stabilizing conjugational effect similar to that in the latter. [Note, however, that hyperconjugation in ethane is only of second order,—see Table III below.] Consideration of the MO's involved indicates, just as in the case of propylene, that hyperconjugation in ethane should have little or no direct effect in restricting free rotation.

Let us consider in some detail the conjugating orbitals in ethane. (The discussion with some simplifications is also applicable to cyanogen and diacetylene.) For simplicity, we may assume a definite symmetry, either D_{3h} (trigonal prism arrangement of the six H atoms) or D_{3d} (center of symmetry). It is simplest first to consider symmetry D_{3h}.

Hyperconjugation in ethane involves interaction among eight electrons which *in the absence of any conjugation* may be assigned to two sets of "$[\pi e]$" C−H bonding MO's, one set localized in each CH_3 group.[15] Or *alternatively*, we may use two nonlocalized sets of MO's which *in the absence of conjugation* may be called "$[\pi+\pi]$" and "$[\pi-\pi]$".[15] Each of the MO's just named has twofold degeneracy, so that four electrons are assigned to it. The problem is similar to that of butadiene, except for the twofold degeneracy here which doubles the number of (here quasi-) unsaturation electrons. This degeneracy is associated with the existence of an axis of symmetry, as in $\mathrm{N{\equiv}C{-}C{\equiv}N}$ and other arrangements with triple bonds, instead of merely a plane of symmetry as in butadiene and other arrangements with double bonds.

Let us call the axis of symmetry the z axis. The x and y axes can in general be assigned arbitrarily so far as azimuth is concerned; however, it will be convenient to choose them so that the yz plane passes through one H atom of each CH_3 group. (Recall that we are assuming symmetry D_{3h}.) We may then designate our quasi-unsaturation MO's $[\pi_x]_{\alpha\beta}$, $[\pi_y]_{\alpha\beta}$, $[\pi_x]_{\gamma\alpha}$, $[\pi_y]_{\gamma\delta}$; or alternatively $[\pi+\pi]_x$, $[\pi+\pi]_y$, and so on. The letters α, β, γ, δ refer to the groups or atoms H_3, C, C, and H_3 in order, so that for instance $[\pi_x]_{\alpha\beta}$ belongs to one CH_3 group, $[\pi_x]_{\gamma\delta}$ to the other. The atoms or groups α, β, γ, δ here are analogous for our purposes to the four similarly-lettered *carbon* atoms in butadiene in Fig. 1 of Paper III. [Whether or not α, β, γ, and δ are on a straight line does not affect the problem in the approximation we are using.] MO's such as $[\pi_x]_{\alpha\beta}$ and $[\pi_y]_{\alpha\beta}$, or $[\pi+\pi]_x$ and $[\pi+\pi]_y$, form degenerate pairs. The subscript x refers to MO's which are antisymmetrical to the yz plane just like the unsaturation MO's in butadiene. The subscript y refers to MO's which are symmetrical to the yz plane, but energetically equivalent in ethane to the corresponding x orbitals because of the axis of symmetry.[15]

Considering first the x orbitals, we note that in the normal state of C_2H_6 there are four electrons which occupy two x MO's analogous to χ_1 and χ_2 of butadiene (cf. III, Eq. (1) and Table II). Similarly, four further electrons occupy two y MO's which again are analogous to χ_1 and χ_2 of butadiene. The C_2H_6 MO's χ_{1x} and χ_{1y} are equal in energy (degenerate) and give over-all bonding, (H_3 to C, C to C (weak), C to CH_3), while the higher energy degenerate pair χ_{2x} and χ_{2y} give $CH_3{-}C$ bonding but weak C−C antibonding. The net effect of conjugation is to tighten the C−H and loosen the C−C bonding somewhat (cf. butadiene, where the original double bonds are weakened and the single bond strengthened). The bonding as a whole is, however, strengthened.

The description just given for $\mathrm{H_3{\equiv}C{-}C{\equiv}H_3}$ applies also, of course, and more directly and simply, to $\mathrm{N{\equiv}C{-}C{\equiv}N}$ and $\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}H}$. In these molecules, the y MO's differ from the x MO's only by a rotation of 90° around the z axis. Also, the conjugation should, of course, be much stronger than in ethane.

We now consider more in detail how the C_2H_6 MO's χ_{1x}, χ_{2x}, χ_{1y}, and χ_{2y} just discussed are related to the MO's called $[\pi e]$, $[\pi+\pi]$, and $[\pi-\pi]$. The orbitals $[\pi_x+\pi_x]$ and $[\pi_x-\pi_x]$, which represent the additive and

[15] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 520 (1935).

the subtractive linear combination of two localized $[\pi_x]$ orbitals one on each CH_3 group, i.e., $[\pi_x]_{\alpha\beta}$ and $[\pi_x]_{\delta\gamma}$, are, respectively, analogous to the butadiene orbitals χ_1 and χ_2 taken *for the case of no conjugation* (the hypothetical "case I" of Tables II–V of III). Similarly with $[\pi_y+\pi_y]$ and $[\pi_y-\pi_y]$, except of course that y-type orbitals are not unsaturation MO's in butadiene.

That is, if we assume *no conjugation* (case I), $\chi_{1x}\equiv[\pi_x+\pi_x]$, $\chi_{2x}\equiv[\pi_x-\pi_x]$, and so on. This case of no conjugation was *tacitly assumed* in the writer's earlier paper on ethane.[15]

The effect of conjugation is to produce distortions within the CH_3-localized $[\pi_x]$ and $[\pi_y]$ orbitals, analogous to those which occur for butadiene in going from case I to case II in Table II of III. These distortions are such as to alter the $C\equiv H_3$ and $C-C$ bonding relations in the way already described. As in the case of butadiene (cf. III, Eq. (1)), we may write

$$\chi_i=\alpha_i\phi_\alpha+\beta_i\phi_\beta+\gamma_i\phi_\gamma+\delta_i\phi_\delta, \qquad (7)$$

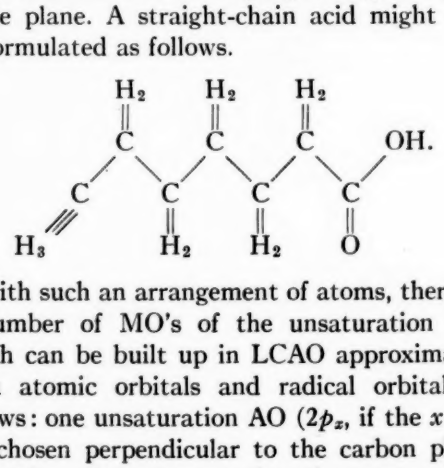
where ϕ_α, ϕ_β, ϕ_γ, ϕ_δ refer, respectively, to suitable orbitals[16] of the H_3 group α, the carbon atom β, the carbon atom γ, and the H_3 group δ. For the carbon atoms, the "suitable orbitals" are $2p_x$ or $2p_y$ AO's. For χ_{1x} and χ_{1y}, the coefficients in Eq. (7) are all positive, with $\alpha_i=\delta_i$ and $\beta_i=\gamma_i$; for χ_{2x} and χ_{2y}, $\delta_i=-\alpha_i$ and $\gamma_i=-\beta_i$. With *no* conjugation, we should have $\alpha_{1x}=\alpha_{1y}=\alpha_{2x}=\alpha_{2y}$, $\beta_{1x}=\beta_{1y}=\beta_{2x}=\beta_{2y}$, but with the α's not quite equal to the β's because of $C-H$ polarity in the $C\equiv H_3$ bonds. (In butadiene, in the approximation used in III, $\alpha_1=\alpha_2=\beta_1=\beta_2=\frac{1}{2}$ in the unconjugated case I.) *With* conjugation, $\alpha_{1x}=\alpha_{1y}$ is decreased, $\beta_{1x}=\beta_{1y}$ increased, while $\alpha_{2x}=\alpha_{2y}$ is increased, $\beta_{2x}=\beta_{2y}$ decreased,—as we see by analogy with the case of butadiene (cf. the coefficients for case II in Table 2 of III). But the changes in the α's and β's through conjugation are doubtless smaller in ethane than in butadiene, that is the hyperconjugation here is weaker, probably much weaker, than the true conjugation in butadiene.

The foregoing discussion of hyperconjugation in ethane assumes symmetry D_{3h}. If we now suppose one CH_3 group rotated by 60° relative to the other (or by 180°, which amounts to the same thing), the symmetry is D_{3d}. We must now reconsider our choice of x and y axes. A convenient new choice is one such that the yz plane still goes through two H atoms, one in each methyl group, the only change being that these two H atoms are now *trans* to each other, whereas with symmetry D_{3h} they were *cis*. With the new x and y axes, the orbitals ϕ_α, ϕ_β, ϕ_γ of the first H_3 group and the two carbon atoms in Eq. (7) are exactly the same as before, but the "suitable orbitals" ϕ_δ of the H_3 group δ are altered.

The new H_3 orbitals ϕ_δ differ from the old, however, only by being turned upside down with respect to the xz plane. [Rotations of 60° or 180° or 300° are all equivalent, since the individual identities of the H atoms do not matter here. A 180° rotation has the same effect as a reflection in the xz plane. It is allowable and convenient to reverse the sign of ϕ_δ after the 180° rotation, so that the original signs for the parts above and below the xz plane are restored.] It is easily seen that, in the approximation we have been using (essentially the Hückel LCAO approximation, cf. III), the coefficients in the various χ's of Eq. (7), and the corresponding energies, are exactly the same now as for symmetry D_{3h}. For intermediate orientations (symmetry D_3) between those having symmetries D_{3h} and D_{3d}, it is less easy to give a proof that the coefficients in Eq. (7) and the energies remain constant, but it seems reasonably clear that any variation is at most very small.

In a higher approximation than that used here, there must be slight differences in the coefficients in Eq. (7) and in the corresponding energies, as one can see qualitatively; but it seems practically certain that such differences are much smaller than the observed potentials hindering free rotation. The cause of the latter must then be looked for elsewhere than in hyperconjugation as treated by the MO approximation. But we see also that the observed hindering potentials are entirely consistent with the existence of appreciable energy effects due to hyperconjugation, which might manifest themselves in other ways than in connection with free rotation.

Another example where hyperconjugation might possibly play a part is that of straight-chain hydrocarbons and their acids. There seems to be evidence that, in their crystals and also in the liquid state,[17] these molecules tend to have their carbon atoms in a zigzag arrangement in a single plane. A straight-chain acid might then be formulated as follows.



With such an arrangement of atoms, there are a number of MO's of the unsaturation type which can be built up in LCAO approximation from atomic orbitals and radical orbitals as follows: one unsaturation AO ($2p_x$, if the x axes are chosen perpendicular to the carbon plane) for each carbon atom and each oxygen atom, and one quasi-unsaturation radical orbital for each H_2 group and for the H_3 group. The H_2 radical orbital is of the type $1s_A-1s_B$ just as in cyclopentadiene (cf. Section 1 and Eq. (2)). It

[16] The suitable H_3 orbitals are given by the writer in J. Chem. Phys. **1**, 495 (1933), Fig. 1*a* and Eqs. (1). In Eqs. (1), the x orbitals for H_3 are of the form $(\alpha-\beta)/2^{\frac{1}{2}}$, the y orbitals of the form $(\alpha+\beta-2\gamma)/6^{\frac{1}{2}}$.

[17] Cf. W. Hückel, *Theoretische Grundlagen der organischen Chemie*, second edition, (Akademische Verlagsgesellschaft M. B. H., 1935) Vol. II, p. 174.

will be seen that a nonbonding $2p_z$ electron pair from the OH group as well as the bonding $2p_z$ pair of the C=O bond enter into the hyperconjugation. [Incidentally, this last interaction of the oxygen $2p_z$ electrons is probably important for the properties of organic acids and their derivatives.]

In molecules of the type just discussed, it looks as if hyperconjugation would tend to stabilize a plane arrangement of the carbon atoms, and to prevent free rotation around the various C−C bonds. For it is easily seen that if the C atoms were not in one plane, but arranged irregularly, or in several planes, the stabilizing effect of extensive over-all hyperconjugation (which may be compared with the stabilizing effect of ordinary conjugation or resonance of double bonds in such plane molecules as diphenyl or triphenylmethyl) would be broken up. Although stabilization of a plane arrangement by hyperconjugation seems likely here, this is not entirely certain, and especially it is, of course, doubtful whether the effect would be of appreciable importance quantitatively.

If hyperconjugation really does help to stabilize the plane arrangement here, and so help to prevent free rotation around C−C bonds, we have a different situation than in propylene and ethane (see above) where we concluded that hyperconjugation probably does *not* interfere with free rotation of a CH_3 group around its axis of symmetry.

8. Hyperconjugation and Bond Distances; Types of Hyperconjugation

According to the electron diffraction studies of Pauling, Brockway and Beach,[18, 19] conjugation causes a considerable shortening of single bonds and a slight lengthening of double (or triple) bonds involved in it. Among triple-bonded molecules, cyanogen and diacetylene have been studied, and behave in this way. Exactly these effects are also predicted by quantum-mechanical calculations of Lennard-Jones (MO method) and Penney (AO method).[20]

Since the theory is qualitatively the same, similar effects should be found when there is hyperconjugation. Since this is surely a weaker thing than ordinary conjugation, appreciable changes in bond distances are not likely to be detectable for the multiple bonds but only for the single bonds involved. Moreover, if hyperconjugation is as universal as it should be according to our discussion in the last section, the ordinary standard C−C single bond distance may already be slightly shorter as a result of hyperconjugation than it would otherwise have been.

With these points in mind, let us examine the available data. The electron diffraction results of Pauling and Brockway[19] show a constant C−C single-bond distance of 1.54A, within the experimental error (±0.01–0.03A), for several saturated hydrocarbons, both open-chain and cyclic, and for alkyl-substituted ethylenes and benzenes. (The value for ethane is slightly above, those for the cyclic compounds are slightly below the average, but the differences are within experimental error.) On the other hand, Herzberg and co-workers[21] obtain a spectroscopic value 1.462±0.005A for the C−C single-bond distance in methylacetylene. Writing this molecule as $H_3{\equiv}C-C{\equiv}C-H$, Herzberg's value would indicate hyperconjugation almost as strong as the conjugation in $N{\equiv}C-C{\equiv}N$ and $HC{\equiv}C-C{\equiv}CH$, where the C−C distance is 1.43A according to electron diffraction data.[18]

If we make allowance for experimental errors, and for the lesser accuracy of the electron diffraction method, the foregoing results on the whole cannot be said to contradict entirely the existence of appreciable effects due to hyperconjugation in the normal states of molecules. This can better be seen if we begin a classification of types of hyperconjugation (see Table III).

First-order hyperconjugations involve one quasi-double or quasi-triple bond (in $C=H_2$ or $C{\equiv}H_3$,—or in $C=R_2$, $C=RH$, or the like) and one true double or triple bond. [A somewhat special branched variety of first-order hyperconjugation is illustrated in cyclopentadiene, where there is hyperconjugation between one $C=H_2$ group and each of *two* (themselves

[18] L. Pauling, L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

[19] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[20] J. E. Lennard-Jones, Proc. Roy. Soc. **A158**, 280 (1937); W. G. Penney, Proc. Roy. Soc. **A158**, 318 (1937).

[21] G. Herzberg, F. Patat and H. Verleger, J. Phys. Chem. **41**, 123 (1937).

TABLE III. *Some types of hyperconjugation.*

TYPE	NUMBER OF ELECTRONS PER HYPER-CONJUGATION	EXAMPLES
First-order double bond hyperconjugation	4	$H_2=C-CH=CH$ (cyclopentadiene) $CH=CH$ $H_3\equiv C-CH=CH_2$ (propylene)
First-order triple bond hyperconjugation	8	$H_3\equiv C-C\equiv CH$ (methylacetylene)
Second-order double bond hyperconjugation	4	$H_2=C-C=H_2$ in cyclopentane $H_2=C\cdots C=H_2$ in ethylene
Second-order triple bond hyperconjugation	8	$H_3\equiv C-C\equiv H_3$ (ethane)

conjugated) double bonds.] Second-order hyperconjugations involve two quasi-double or -triple bonds. Ordinary conjugations (of which several varieties are mentioned in Section 1) fit into the scheme under the heading of zero-order conjugations.

A quasi-triple bond as in $C\equiv H_3$ gives triple bond hyperconjugation only with another real or quasi-triple bond. With a real or quasi-double bond it gives only double bond hyperconjugation (example, propylene).

It seems likely that first-order hyperconjugations should produce larger effects than second-order ones. Triple bond hyperconjugations should produce considerably larger effects than double bond ones, since they involve twice as many electrons but are otherwise similar.

We now note that methylacetylene, where a large decrease of the C−C distance is observed, belongs precisely to the type in Table III for which the largest effects are expected. On the other hand, the methyl-substituted benzenes and alkyl-substituted ethylenes, which show no appreciable lowering in C−C distance according to Pauling and Brockway, belong to the second most favorable class (the first-order double bond type). The results for them, therefore, indicate that any effects of hyperconjugation on bond distance even in such relatively favorable cases are not larger than the errors inherent in the electron-diffraction method. This is in harmony with the considerations advanced at the end of Sections 4 and 6, and in Section 7, regarding the relative importance of hyperconjugation for normal and excited states. But the small C−C bond distance in methylacetylene seems to constitute evidence for a large effect even in the normal state.

In conclusion, the writer wishes to thank Professor W. G. Brown for helpful discussion and the suggestion of the word hyperconjugation,[4, 5] and Professor G. B. Kistiakowsky for helpful correspondence.

Intensities of Electronic Transitions in Molecular Spectra

V. Benzene

ROBERT S. MULLIKEN
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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The spectrum of benzene is discussed. According to the calculations, the strong $N \rightarrow V$ absorption region near and just below λ2000 should be stronger than for a molecule with three unconjugated double bonds. New quantitative measurements on the spectrum near and below λ2000 would be of interest. Relations of the spectra of pyridine and of benzene derivatives to that of benzene are briefly discussed.

1. BENZENE

THE $N \rightarrow V$ spectrum for the mobile electrons of benzene has already been discussed briefly in II of this series,[1] and to a slight extent in III.[2] Details will now be given. The problem is not essentially different from that of butadiene. The principal changes are (1) that conjugation of the (here three) double bonds is stronger because of the more favorable conditions for resonance; (2) that the high symmetry of the molecule causes a simplification so that there is here only one allowed $N \rightarrow V$ transition, instead of two as in transbutadiene or four as in cisbutadiene.

Certain additional weak electronic transitions, particularly the well-known absorption region near λ2600 can, however, rightly be classified as additional but forbidden $N \rightarrow V$ transitions (cf. also Section 2). According to Sklar,[3] the λ2600 transition is one forbidden by the electronic selection rules, namely $N \rightarrow {}^1B_{2u}$ of Eq. (10) below. The fact that it nevertheless occurs, with low intensity, can be explained through perturbations of the Herzberg-Teller type. The λ2600 transition must then "steal" a little intensity from other allowed transitions, probably mostly from the allowed $N \rightarrow V$ transition, which occurs in the region about λ2100–1700. In addition to the λ2600 forbidden transition, there should also be another similar one ($N \rightarrow {}^1B_{1u}$ of Eq. (10)), but according to Sklar's calculations, this probably occurs at much shorter wave-lengths. In the present connection it is of interest to point out also that in pyridine and in many benzene derivatives the analogs of these $N \rightarrow {}^1B_{1u}$ and $N \rightarrow {}^1B_{2u}$ transitions are no longer forbidden, and may be considered as normal members of the $N \rightarrow V$ family (cf. Section 2).

The calculations on $N \rightarrow V$ now to be made will be carried through only in LCAO MO approximation. Proceeding just as in Section 2 of III for butadiene, we consider just the six unsaturation electrons. Let the six carbon atoms be lettered as in Fig. 1, and the corresponding $2p_z$ carbon AO's be called ϕ_α, ϕ_β, and so on. From these, six linearly independent LCAO MO's can be constructed, all of which can be specified in the following form:

$$\chi_i = \alpha_i\phi_\alpha + \beta_i\phi_\beta + \gamma_i\phi_\gamma + \delta_i\phi_\delta + \epsilon_i\phi_\epsilon + \eta_i\phi_\eta. \quad (1)$$

The values of the coefficients for the six χ's are listed in Table I. In the case of the degenerate pair χ_2, χ_3, the coefficients are, of course, not unique but the choice made is one which is convenient for our purpose, using real forms. The same applies to the degenerate pair χ_4, χ_5.

In the normal state of benzene, χ_1, χ_2, and χ_3 are each occupied by two electrons (cf. (2)). We next consider the V and T states, which can be obtained by excitation of a single electron into one of the normally unoccupied MO's χ_4, χ_5, and χ_6. These are given in (2). Many other excited states could be obtained by simultaneous excitation of two or more unsaturation electrons, but we need not concern ourselves with these, since spectroscopic transitions to them must be weak, being forbidden in MO approximation.

[1] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939): II of this series.
[2] R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939): III of this series.
[3] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

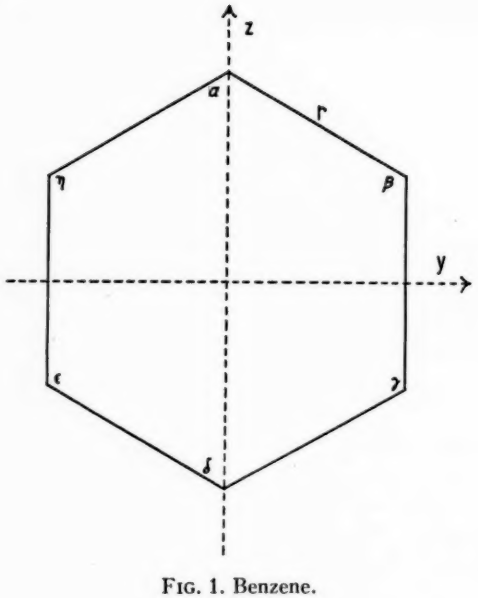

FIG. 1. Benzene.

$$\left.\begin{array}{l} N\text{: } (\chi_1)^2(\chi_2)^2(\chi_3^2),\ {}^1A_{1g} \\ V \text{ and } T \text{ states: } (\chi_1)^2(\chi_{2,3})^3(\chi_{4,5}), \\ \qquad {}^3B_{1u},\ {}^3B_{2u},\ {}^3E_{1u},\ {}^1B_{1u},\ {}^1B_{2u},\ {}^1E_{1u} \\ V \text{ and } T \text{ states: } \begin{cases} (\chi_1)^2(\chi_{2,3})^3(\chi_6),\ {}^3E_{2g},\ {}^1E_{2g} \\ \chi_1(\chi_2)^2(\chi_3)^2(\chi_{4,5}),\ {}^3E_{2g},\ {}^1E_{2g} \end{cases} \\ V \text{ and } T \text{ states: } (\chi_1)(\chi_2)^2(\chi_3)^2(\chi_6),\ {}^3B_{1u},\ {}^1B_{1u}. \end{array}\right\} \quad (2)$$

The energies of all the states in the second line of (2) have been calculated in LCAO as well as in AO approximation by Sklar and Goeppert-Mayer.[3] From the electronic selection rules for molecules of symmetry D_{6h},[4] it is readily shown that transitions from state N to all the excited states in (2) are forbidden, except only to the ${}^1E_{1u}$, which moreover can be identified a V state.[1]

In (2), the symbols $\chi_{2,3}$ and $\chi_{4,5}$ refer to the two degenerate pairs of orbitals χ_2, χ_3 and χ_4, χ_5 of Table I. When such degeneracy is present in the MO's, one cannot in general specify a single electron configuration for each state in terms of the orbitals χ_2, χ_3, χ_4, and χ_5. We are, of course, now interested primarily only in the $V\,{}^1E_{1u}$ state. We need its wave functions (of which two independent ones can be obtained, since the state has twofold degeneracy) in order to calculate the intensity of the transition $N \rightarrow V$. For the purpose of obtaining the desired wave functions, let us consider a set of hypothetical states with electron configurations as follows:

$$\left.\begin{array}{l} (\chi_1)^2(\chi_2)(\chi_3)^2(\chi_5),\ {}^{1,3}Y \\ (\chi_1)^2(\chi_2)^2(\chi_3)(\chi_4),\ {}^{1,3}Y' \\ (\chi_1)^2(\chi_2)(\chi_3)^2(\chi_4),\ {}^{1,3}Z \\ (\chi_1)^2(\chi_2)^2(\chi_3)(\chi_5),\ {}^{1,3}Z'. \end{array}\right\} \quad (3)$$

A transition from state N to the hypothetical state ${}^1Y$ (cf. (2) and (3)) would involve transition of a single electron from the χ_2 to the χ_5 MO, leaving a second electron in χ_2; all other electrons remain in closed shells. The dipole strength Q of $N \rightarrow {}^1Y$ is found (see below) to be y-polarized (see Fig. 1 for y and z axes). It is given by

$$Q(N \rightarrow {}^1Y) = \int \psi_N (y_1 + y_2) \psi_{1Y} d\tau, \quad (4)$$

where y_1 and y_2 refer to the two electrons which are initially in the χ_2 shell. This reduces (cf. discussion in Section 3 of III for justification of Eqs. (4) and (5)) to

$$Q(N \rightarrow {}^1Y) = 2^{\frac{1}{2}} \int \chi_2 y \chi_5 dv. \quad (5)$$

Putting in the proper expressions for χ_2 and χ_5 based on Eq. (1) and Table I, we get

$$Q(N \rightarrow {}^1Y) = 6^{-\frac{1}{2}}(y_\beta - y_\eta) = r/2^{\frac{1}{2}}, \quad (6)$$

where r is the distance between any two adjacent carbon atoms of the benzene hexagon (cf. Fig. 1). That the transition $N \rightarrow {}^1Y$ is y-polarized is easily seen by substituting z_1+z_2 for y_1+y_2 in Eq. (4), and proceeding as above; this leads to $Q_z = 0$.

TABLE I. *Forms and energies of LCAO MO's of benzene.*

NAME OF MO[1]	COEFFICIENTS IN EQ. (1)[2,3]						ENERGY[2]
	α_i	β_i	γ_i	δ_i	ϵ_i	η_i	
$\chi_1 a_{2u}$	a	a	a	a	a	a	$C-2\epsilon$
$\chi_2 e_{1g}$	b	$b/2$	$-b/2$	$-b$	$-b/2$	$b/2$	$C-\epsilon$
$\chi_3 e_{1g}$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	$C-\epsilon$
$\chi_4 e_{2u}$	b	$-b/2$	$-b/2$	b	$-b/2$	$-b/2$	$C+\epsilon$
$\chi_5 e_{2u}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	$C+\epsilon$
$\chi_6 b_{2g}$	a	$-a$	a	$-a$	a	$-a$	$C+2\epsilon$

[1] The designations of the orbitals are in accordance with the modified Placzek system proposed by the writer in Phys. Rev. **43**, 288 (1933), except that (following Wilson, Goeppert-Mayer, and Sklar[3]), Tisza's symbols (Zeits. f. Physik **82**, 48 (1933)) e_1 and e_2 are, respectively, used in place of the writer's cumbersome e_x^* and e^*.

[2] See E. Hückel, Zeits. f. Physik **70**, 242 (1931); except that real χ's are here used, obtained by suitably combining the complex χ's given by Hückel.

[3] The quantities a and b are $6^{-\frac{1}{2}}$ and $3^{-\frac{1}{2}}$, respectively. The χ's are then all correctly normalized except for neglect of overlapping integrals. This, however, makes only an unimportant difference in our results.

[4] Cf. R. S. Mulliken, Phys. Rev. **43**, 288 (1933).

[In arriving at Eq. (6), certain cross integrals have been neglected, but the neglect of these and of overlapping integrals in the coefficients of Table I (cf. Table I, note 3), is unimportant. This neglect means that Eq. (6) is analogous to Eq. (11a), and not to Eq. (11), of Paper II.]

In the same way as for Eq. (6) we obtain the further relations:

$$Q(N\rightarrow{}^1Y)=Q(N\rightarrow{}^1Y')$$
$$=Q(N\rightarrow{}^1Z)=Q(N\rightarrow{}^1Z')=r/2^{\frac{1}{2}}. \quad (7)$$

The $N\rightarrow{}^1Y$ and $N\rightarrow{}^1Y'$ transitions are y-polarized, the other two z-polarized. We now inquire what relation these results have to the desired Q values for the actual transition $N\rightarrow V\,{}^1E_u$.

The states ${}^1Y$, ${}^1Y'$, ${}^1Z$, ${}^1Z'$ are not real molecular states, but it can be shown (see below) that their wave functions are related in the following way to the true wave functions:

$$\left.\begin{aligned}\psi_y({}^1E_{1u}),\ \psi({}^1B_{1u})&=[\psi({}^1Y)\pm\psi({}^1Y')]/2^{\frac{1}{2}},\\ \psi_z({}^1E_{1u}),\ \psi({}^1B_{2u})&=[\psi({}^1Z)\pm\psi({}^1Z')]/2^{\frac{1}{2}}.\end{aligned}\right\} \quad (8)$$

The + signs go with two functions which represent a convenient choice for the two degenerate ${}^1E_{1u}$ functions; these two may be called $\psi_y({}^1E_{1u})$ and $\psi_z({}^1E_{1u})$ since their behavior under the operations of the D_{6h} symmetry group is easily shown by trial to be like that of the coordinates y and z. Using Eqs. (4), (5), it is easily seen that

$$Q_y(N\rightarrow V\,{}^1E_{1u})=Q_z(N\rightarrow V\,{}^1E_{1u})=r; \quad (9)$$

also, as expected from the selection rules,

$$Q(N\rightarrow{}^1B_{1u})=Q(N\rightarrow{}^1B_{2u})=0, \quad (10)$$

for the ${}^1B_{1u}$ and ${}^1B_{2u}$ wave functions given by Eqs. (8). In fact, the proper linear combinations given in Eqs. (8) are most easily determined by choosing them so that Eqs. (10) shall be true, thus satisfying the selection rules (cf. also reference 3). According to Sklar,[3] the λ2600 absorption-region in benzene represents the forbidden transition $N\rightarrow{}^1B_{2u}$; the $N\rightarrow{}^1B_{1u}$ then occurs probably well below λ2000.

Since $Q_y=Q_z=r$ for $N\rightarrow V$ in benzene according to Eqs. (9), the total Q^2 for the transition is

$$Q^2(N\rightarrow V)=Q_y{}^2+Q_z{}^2=2r^2. \quad (11)$$

Referring to Section 4 of III, we note that for three unconjugated double bonds in the same approximation, the total Q^2 would be $3r^2/2$. Hence the calculated effect of conjugation in benzene is to increase Q^2 in the ratio 4/3. This fractional increase is about halfway between those which we arrived at for cis- and for transbutadiene with $\theta=30°$ in Table IV of III. Unlike the case of butadiene, the calculated result here does not involve simplifying assumptions beyond the use of the LCAO approximation and the neglect of overlapping integrals. It is also more definite in that there are no *cis*, *trans* alternatives and no questions about θ. In the writer's opinion, the predicted relative increase in Q^2 by conjugation is probably at least qualitatively reliable, although as we know from II and III, the *absolute* Q^2 values calculated for $N\rightarrow V$ transitions by the LCAO method are too large.

TABLE II. *Experimental data on cyclic trienes.*

Substance	State	Observer[1]	ν_{max}	$\nu_{max}(N\rightarrow V)$	$f(N\rightarrow V)$[2]
Benzene	Vapor	CS		51,000, *56,000*	(51,000 weaker) (56,000 stronger)
	Hexane sol.	ICT	39,000 (f=0.0006)	50,500, ——	0.05, ——
Pyridine	Hexane sol.	ICT	39,500 (f=0.02)	Below 50,000	——

[1] CS refers to E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 763 (1936), and cf. also discussion in II of this series; ICT refers to *International Critical Tables*, Vol. 5, Fig. 21 or 33. In regard to benzene, see also N. Q. Chako, J. Chem. Phys. **2**, 648 (1934). The intensity data for benzene seem to be somewhat conflicting, but in any case the available quantitative data and the f value given in the table for $N\rightarrow V$ refer only to a part of the weaker longer wave-length portion of the $N\rightarrow V$ region (cf. discussion in II of this series).

[2] Cf. Paper III, Table VI, footnote 4 for explanation of f values.

On substituting the experimental r=1.39A into Eq. (11), we find

$$Q^2(N\rightarrow V)=3.86\text{A}^2. \quad (12)$$

Taking ν for $N\rightarrow V$ as 56,000 (cf. Table II; also Paper II, Section 5), we calculate by Eq. (I, 9), using $G'=2$ but $D=Q_y{}^2=Q_z{}^2=Q^2/2$,

$$f(N\rightarrow V)=2.37. \quad (13)$$

In accordance with previous experience,[1, 2] f of Eq. (13) should be multiplied by an empirical correction factor of about 0.2 or 0.3. (The factor $\frac{1}{3}$ was found for O_2 in II, and 0.25 for the open-chain dienes in III. Unfortunately no adequate quantitative absorption data are available for benzene (cf. Table II, and discussion in II of this

series, Section 5). New quantitative measurements on the $N \rightarrow V$ absorption region in benzene would be extremely interesting.

2. Benzene Derivatives and Pyridine

We may conveniently note at this point that distortions of shape or charge distribution in the benzene ring, if of suitable symmetry, should cause transfer of a small fraction of the large $N \rightarrow V$ intensity to the transitions $N \rightarrow {}^1B_{1u}$ and $N \rightarrow {}^1B_{2u}$ of Eq. (10), which are forbidden in benzene (cf. Section 1, paragraph two). When this happens, the ${}^1B_{1u}$ and ${}^1B_{2u}$ states which, as Sklar has shown,[3] are partially (${}^1B_{2u}$) or mostly (${}^1B_{1u}$) non-ionic in AO approximation, may be considered as perturbed by the ionic state ${}^1E_{1u}$. (At the same time, the ${}^1E_{1u}$ state is split into two nondegenerate states.)

There appear to be interesting possibilities for perturbation calculations and experimental studies here, since the intensities of $N \rightarrow {}^1B_{1u}$ and $N \rightarrow {}^1B_{2u}$ may be very sensitive to substitutions in the ring. A still more pronounced effect might be expected in pyridine, where we have not just a substitution of a ring hydrogen, but the replacement of a CH group by a nitrogen atom. In agreement with this, it is known experimentally (cf. Table II, fourth column), that the pyridine absorption region near λ2600 is about thirty times as intense as the otherwise very similar and without much doubt analogous λ2600 region in benzene which Sklar has attributed to the forbidden $N \rightarrow {}^1B_{2u}$ transition.

If substitution of ring hydrogen atoms introduces conjugation between substituent groups and the ring, changes in the spectrum should be more radical.

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Intensities of Electronic Transitions in Molecular Spectra

VI. Molecular Refractivities of Organic Compounds

Robert S. Mulliken
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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In connection with intensity calculations on the spectra of dienes and other compounds in III, IV and V of this series, a study is made of molecular refractivities. Rough theoretical calculations are made on the partial refractivities for the unsaturation electrons in open-chain and cyclic dienes (particularly conjugated dienes) and in benzene. The observed *exaltations* of the refractivity and dispersion in open-chain conjugated dienes appear to be satisfactorily explained qualitatively, and to a certain extent semi-quantitatively, by the rough calculations. Exaitations in other conjugated systems (e.g. systems with conjugated triple bonds, or with conjugation of C=O and C=C bonds) can be explained along similar lines. The refractivity data on unconjugated alkenes and dienes and on the conjugated cyclic dienes appear also to be in harmony with the theory. The considerable effects of alkyl substitution on the exaltation in substituted butadienes, benzenes, and styrols are attributed to hyperconjugation. Saturated compounds are briefly discussed in Section 4.

1. Introduction

In III, IV and V of this series theoretical calculations were made of intensities in the "$N \rightarrow V$" ultraviolet absorption spectra of dienes and related compounds, and found to be closely correlated with the rather incomplete experimental data.[1, 2] By a slight extension of the same

[1] R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939): III of this series.
[2] R. S. Mulliken, J. Chem. Phys. **7**, 339, 353 (1939): IV and V of this series.

calculations, it is possible to make significant predictions concerning refractive indices and dispersion.

The problem of the relations between absorption spectra and refractive indices has already been discussed in papers by Lowry and Alsopp,[3] and by others.[4] Among other things, Lowry and Alsopp have from empirical data reached conclusions similar to the present ones as to the relation between *cis* or *trans* molecule form and molecular refractivity in conjugated dienes. They also discuss dispersion. The present work goes beyond that of Lowry and Alsopp because of the theoretical calculations carried out in III, which are here extensively utilized, and in certain other respects.

In the present paper, emphasis is placed on refractivities for a definite wave-length, since it appears that empirical formulas representing dispersion data commonly prove unreliable when one tries to correlate them with information on absorption bands. Nevertheless, the theoretical calculations on which the present work is based are applicable to the explanation and prediction of dispersion curves. They should also be applicable in explaining and predicting polarizabilities of molecules. These subjects will not, however, be taken up explicitly in the present paper.

According to classical theory, the "molecular refractivity" M is given, for frequencies ν at which there is no appreciable absorption, by the Lorenz-Lorentz formula[4]

$$\left.\begin{aligned} M &\equiv [(n^2-1)/(n^2+2)\mu/d] \\ &= (Ae^2/3\pi mc^2)\sum_j f_{Nj}/(\nu_{Nj}^2-\nu^2) \\ &= 1.80\times 10^{10}\sum_j f_{Nj}/(\nu_{Nj}^2-\nu^2) \end{aligned}\right\}. \quad (1)$$

Here n is the index of refraction, μ the molecular weight, d the density, and A Avogadro's number; ν is the frequency at which the refraction is measured, and f_{Nj} is the strength (in terms of effective number of dispersion electrons) of the absorption region whose maximum of absorption is at ν_{Nj}. The ν's are to be taken in cm^{-1}. In Eq. (1), the usual sum rule for the f's holds (the sum

[3] T. M. Lowry and C. B. Alsopp, Proc. Roy. Soc. **163A**, 356 (1937), and earlier papers. In Table II, on p. 361, the ϵ_{max} values attributed to Smakula should all be divided by 2.30; and the data for "hexadiene (2 : 4)" should be assigned to β,γ-dimethylbutadiene.

[4] For a discussion of molecular refractivities of organic compounds, cf. W. Hückel, *Theoretische Grundlagen der organischen Chemie* (Akademische Verlagsgesellschaft M. B. H., Leipzig, 1935), second edition, Vol. 2, pp. 83–106; 139–158 tables. See also H. Gilman, *Organic Chemistry* (John Wiley & Sons, New York, 1938), Vol. 2, pp. 1737–1742 for discussion, and reference 15 for data.

TABLE I. *Experimental values of molecular refractivity M_D for dienes and cyclic trienes.*

Molecule	M_D Values: Total*	Partial Refractivity Due to Unsaturation Electrons**	Normal Unsaturation-electron Partial Refractivity for Zero Conjugation†	Exaltation E*
1,5-hexadiene (diallyl)	29.08±.05	5.99	5.88	+0.11
1,3-butadiene	21.1±0.1	7.3	5.88	+1.4
1,3-pentadiene	25.8±0.1	7.3	5.88	+1.4
2,4-hexadiene	30.81±.05	7.72	5.88	+1.84
2,4-heptadiene	35.6±0.1	7.9	5.88	+2.0
β-methyl-1,3-butadiene (isoprene)	25.41±.05	6.93	5.88	+1.04
β,γ-dimethyl-1,3-butadiene	29.72±.05	6.63	5.88	+0.75
cyclopentadiene	21.85±.05	5.57	5.88	−0.31
1,3-cyclohexadiene	26.74±.05	5.85	5.88	−0.03
1,3-cycloheptadiene	31.69(H_α)±.05	6.27(H_α)	5.78	+0.49
cyclohexatriene (benzene)	26.14±.005	8.65	8.82	−0.17
methylbenzene (toluene)	31.09±.005	8.99	8.82	+0.17
sym. trimethylbenzene (mesitylene)	40.79±.05	9.45	8.82	+0.63

* These data are taken from reference 15.

** The values given for the unsaturation electrons are obtained by taking 2.942 N_x+E (cf. Eq. (1)). In the case of 1,3-cycloheptadiene the data are for H_α instead of sodium D light (cf. Hückel, reference 4).

† The "normal unsaturation-electron partial refractivity for zero conjugation" values are given by 2.942N_x.

TABLE II. *Calculated partial molecular refractivity ΔM due to $N \rightarrow V$ transitions of unsaturation electrons in 1,3-butadiene (LCAO approximation).**

Refracted Frequency	Case I** (No conjugation)	Case II (conjugated)**			
		Cis, $\theta=0°$	*Cis*, 20°	*Cis*, 30°	*Trans*, 30°
0	6.21	6.28	7.52	8.32	10.40
15233(H_α)	6.68	6.74	8.18	9.11	11.57
16965(NaD)	6.82	6.87	8.38	9.34	11.91
20565(H_β)	7.13	7.18	8.83	9.89	12.74
23033(H_γ)	7.42	7.47	9.26	10.41	13.55

* The calculations were made using just the *four terms* of the summation, in the right side of Eq. (1), corresponding to the four $N \rightarrow V$ transitions, with f_{NV} and ν_{NV} values as given in Table V of III.

** For the meaning of Cases I and II, see III of this series; for θ, see Fig. 1 of III.

of the f's is equal to the total number of electrons in the molecule).

Strictly speaking, Eq. (1) should be used only for vapors. In practice, however, nearly the same M values are usually obtained when it is applied to liquids.[5] Since the present calculations involve rough approximations, it should be justifiable to use Eq. (1) for liquids, and we shall do so.

2. Open-Chain Conjugated Dienes

Existing empirical data on the molecular refractivities of polyenes can be summarized in the following equation:[6]

$$M_D = 1.705N_{C-H} + 1.209N_{C-C} + 2.942N_x + E, \quad (2)$$

where N_{C-H} is the number of C−H bonds, N_{C-C} the number of C−C bonds (including a count of one for each double bond), N_x the number of unsaturation-electron[2] bonds (that is, a count of one for each double bond), and E is the "exaltation" of the molecular refractivity, a quantity which takes care of departures of observed M_D values from those calculated from Eq. (2) with E omitted. Eq. (2) without E represents an *average* behavior for hydrocarbon molecules containing single and double bonds. The quantity E shows particularly large positive values for compounds containing conjugated double bonds (cf. Table I). M_D is the value of M for $\nu = 16{,}965$ (sodium D lines).

It will be noted that the largest coefficient in Eq. (2) is that of N_x; also, the largest and most varying values of E occur for molecules with double bonds. It is thus seen empirically that M is peculiarly sensitive to the presence and the condition of the unsaturation electrons. In the following, this sensitiveness and this variability receive a theoretical explanation.

The calculations to be made will concern only the partial refractivities of (i.e., the *contributions* made to M by) the unsaturation electrons. In making comparisons with empirical data, we shall in general tacitly assume that the quantity E in Eq. (2) is due entirely to the unsaturation electrons. Actually, of course, part of E should in general be attributed to the other electrons (see especially the end of Section 6, below); failure to allow for this will merely increase somewhat the errors of our at best rough comparisons of experiment with theory.

In order to calculate the unsaturation-electron partial refractivity for any molecule, we use just those terms of Eq. (1) which correspond to absorption of light by unsaturation electrons. In order to do this, we need to know the f_{Nj}'s and the ν_{Nj}'s for all unsaturation electron transitions.

Among the most important transitions of this sort are the $N \rightarrow V$ transitions discussed in III, IV and V of this series. The necessary quantities f_{Nj} and ν_{Nj} (where N stands for the normal, j for one of the V states) have already been calculated theoretically in LCAO MO approximation for the case of no conjugation and for several models of 1,3-butadiene, and are given in Table V of III (*q.v.*). As discussed in III, the results for butadiene should in general be applicable also to *derivatives* of this substance; but as we have seen in IV (see also Section 6 below), corrections are required

TABLE III. *Mean effective frequencies[7] in cm^{-1} for refraction of sodium D lines.*

C−H Bond	C−C Bond	C−C Unsaturation-electron Bond (Not Conjugated)
1.463×10^5	1.735×10^5	1.120×10^5

[5] Eq. (1) would be applicable to liquids as well as vapors if the liquid were polarized like an isotropic medium by light of frequency ν (Lorenz-Lorentz forces). Empirically, according to Hückel (reference 4, top of p. 85 and of p. 103), M (defined by the left side of Eq. (1)) is just slightly larger for a given substance in the vapor than in the liquid state.

[6] This is easily obtained on the basis of W. Hückel's review in reference 4. The coefficients in Eq. (2) arise almost entirely from the refractivities of the valence electrons, but do also contain very small contributions due to the carbon 1*s* electrons.

when hyperconjugation is present, as for example in the cyclic dienes.

Using the f_{NV} and ν_{NV} values of III, Table V, for the four $N \rightarrow V$ transitions which are predicted in dienes, the partial refractivity ΔM due to the unsaturation-electron $N \rightarrow V$ transitions has been calculated using Eq. (1), for each of several values of ν, and for each of several molecular models. The results are given in Table II.

Before examining Tables I and II, it will be desirable to return to Eq. (2), and to calculate a "mean effective frequency" for the partial refractivity associated with each of the three types of bonds which are covered by the equation. To explain what is meant by "mean effective frequency" for a single type of bond, let us take the hypothetical case of a molecule with just one bond, for example a C−H bond. Then $M_D = 1.705$ by Eq. (2). Now by Eq. (1), we should have for our hypothetical case,

$$1.705 = 1.80 \times 10^{10} \sum_j f_{Nj}/(\nu_{Nj}^2 - \nu_D^2), \qquad (3)$$

where $\nu_D = 0.170 \times 10^5$. Our mean effective C−H bond frequency ν_{ef} (for sodium D light) is such a frequency that if the summation in Eq. (3) be replaced by a single term $f/(\nu_{ef}^2 - \nu_D^2)$, with f put equal to *two* since there are two electrons per bond, the resulting modified Eq. (3) is satisfied.[7] The values of ν_{ef} obtained in this way are listed in Table III. [For other refracted frequencies than ν_D, the ν_{ef} values would be slightly different.] In case there is an E in Eq. (2) and this is attributed to the unsaturation electrons, the ν_{ef} for the latter should be altered accordingly (the alteration would usually not be large).

It is of interest to compare the effective frequencies in Table III with ionization frequencies. The mean ionization frequencies for the C−H bond, the ordinary C−C bond, and the C−C unsaturation-electron bond, are probably roughly 1.15×10^5, 1.0×10^5, and 0.9×10^5, respectively.[8] Thus the effective frequencies in Table III correspond to values in excess of the ionization potentials,—as is a general rule for such frequencies.[9] However, the excess is seen to be smallest in the case of the unsaturation electrons (still smaller if there is exaltation due to conjugation). This is an indication that absorption at long wave-lengths is relatively more important for the unsaturation electrons than for the others.

Referring now to Table I, we see that the partial refractivity attributable to the four unsaturation electrons, in the various dienes listed, varies between 5.57 and 7.85. Comparing these values with the calculated partial refractivities ΔM_D corresponding to the $N \rightarrow V$ transitions (Table II), we note that they are of the same order of magnitude. However, the calculated values are larger than the observed, whereas to be correct they would necessarily be *smaller*, since only a *part* of the whole unsaturation-electron partial refractivity can arise from the $N \rightarrow V$ transitions. This is not at all discouraging, however, for as we have seen previ-

TABLE IV. *Estimated partial molecular refractivities ΔM_D due to $N \rightarrow V$ transitions of the unsaturation electrons in dienes and cyclic trienes.*

EXPERIMENTAL*, †		CALCULATED**, †
diallyl (unconjugated):	1.62	
β,γ-dimethylbutadiene:	2.33	
isoprene (β-methylbutadiene):	2.63	no conjugation: 1.71
1,3-butadiene:	3.0	cis-forms, $\theta = 0°$: 1.72
1,3-pentadiene:	3.0	
2,4-hexadiene:	3.44	cis-forms, $\theta = 20°$: 2.10
2,4-heptadiene:	3.6	
		cis-forms, $\theta = 30°$: 2.34
cyclopentadiene:	1.26	
cyclohexadiene:	1.53	trans-forms, $\theta = 30°$: 2.98
cycloheptadiene:	2.06	
		benzene: 3.73
benzene:	2.30	
toluene (methylbenzene):	2.64	
mesitylene (sym. trimethylbenzene):	3.10	

* The "experimental" values for dienes are obtained by subtracting quantities ranging from 4.37 to 4.28 (see text) from the unsaturation-electron partial refractivity values given in column 3 of Table I; in the case where data are given only for H_α in Table I, a suitable estimated correction has been made.

** The "calculated" values for dienes are taken as just 0.25 time the semi-theoretical LCAO values of Table II; they correspond to total f strengths of from 0.28 to 0.35.

† The "experimental" value for benzene and its derivatives is obtained in the same way, except that the quantity 6.35 (see text) is subtracted from the unsaturation-electron partial refractivity value of Table I. The "calculated" value for benzene is obtained as described in the text, using the same correction factor 0.25 as for the dienes.

[7] Our calculated mean effective frequencies for the bonding electrons are slightly in error due to neglect of the carbon K electrons (reference 6).

[8] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 518 (1935). Note that in general there is more than one ionization potential for each type of bond; especially for the unsaturation electrons in a conjugated or resonating polyene there must be a considerable range of values; but the *average* of the several ionization potentials for a given type of bond in a complex molecule should be more or less constant from molecule to molecule, and not very greatly affected by resonance or conjugation.

[9] Cf. K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik XX* (J. Springer, Berlin, 1928), pp. 626–8.

ously in II and III of this series, the LCAO semi-theoretical f values[10] are considerably too large, so that the calculated ΔM values must be too large in the same proportion. In studying absorption spectra in III we found agreement with experiment by multiplying the semi-theoretical f values by an empirical factor of about 0.25. Let us try the same factor here for the ΔM values of Table II.

Using the factor 0.25, the total calculated f strength of the four $N \rightarrow V$ transitions in Table V of III ranges from 0.28 to 0.35. This would mean that an oscillator strength of between 3.72 and 3.65 electrons (since there are altogether four unsaturation electrons in the dienes) must belong to *other* transitions, including partly Rydberg series transitions but evidently comprising mostly photo-ionization transitions in view of the high mean effective frequency in Table III. After deducting the $N \rightarrow V$ low frequency contribution to the refraction, the *remaining* part must have a higher mean effective frequency than the Table III mean. As a fairly reasonable estimate (found by trial and error to give good results in Table IV), suppose we assume that this high frequency contribution has a mean effective ν of 1.25×10^5. Putting this into Eq. (1), with $f = 3.72$ to 3.65 (depending on the presumed shape of the molecule), we find from 4.37 to 4.28 as the corresponding partial molecular refractivity for sodium D light.

Now if we subtract quantities ranging from 4.37 to 4.28 from each of the partial M_D values in the third column of Table I, the remainder in each case may be taken as a rough experimental value for that part of the refractivity which is associated with the $N \rightarrow V$ transitions of the unsaturation electrons. As corresponding theoretical values we take the Table II values each multiplied by a factor 0.25. The comparison is made in Table IV.

The roughly quantitative agreement between the "experimental" and the "calculated" ranges of values in Table IV strongly encourages the view, already indicated by absorption data in III, that a considerable part of the large partial refractivity due to the unsaturation electrons is attributable to the $N \rightarrow V$ transitions of these electrons. Further, if we suppose that 1,3-butadiene and its end-substituted derivatives 1,3-pentadiene, 2,4-hexadiene and 2,4-heptadiene are *trans*, but that the centrally-substituted derivatives isoprene and especially β,γ-dimethyl butadiene are partly or wholly *cis*, the "experimental" values are seen to be in rough agreement with the calculated values. This supports the suggestion of W. Hückel[11] and of Lowry and Alsopp[3] that large exaltation of the refractivity is favored by the *trans* position. It is also fairly well in accord with the conclusions of III on absorption spectra. However, it does not give a satisfactory explanation of the pronounced variation of the exaltation with the number of substituted alkyl groups, and as we shall see in Section 6, it is likely that the correct explanation is not in terms of *cis-trans* isomerism, but of hyperconjugation.

3. Miscellaneous Unsaturated Types

In passing, it may be mentioned that the observed exaltations of refractivity which occur when triple bonds are conjugated should be explainable by the same methods as are used here for substances with conjugated double bonds (cf. IV, Section 7 for triple bond theory; and v. Auwers, citation in IV, Table I, reference 1, for refractivity data). The exaltations which occur when C=O bonds are conjugated with C=C bonds are also explainable along the same lines as here.

Referring again to Table IV, one sees that the calculated value for the case of *no* conjugation agrees fairly well with the experimental value for a typical example of an unconjugated diene (namely diallyl). All this tends to show that our theoretical explanation is on the right track.

4. Critical Discussion. Saturated Compounds

It should be remembered, however, that the roughly quantitative agreements obtained are partly a result of empirical or *ad hoc* adjustment of certain parameters. Particularly *ad hoc* is the assumed mean effective frequency for that part of the unsaturation-electron partial refractivity

[10] "Semi-theoretical" f values are based on theoretically calculated values of the dipole-strength Q^2 combined with empirical (or semi-empirical) ν values: cf. reference 2 in III of this series.

[11] W. Hückel, reference 4, p. 94 footnote.

not belonging to $N \rightarrow V$ transitions. The empirical factor 0.25 introduced to correct the Table II ΔM_D values is also somewhat doubtful. [It may be noted here that if we had used the presumably rougher Hückel approximation instead of the Lennard-Jones approximation, we should have got somewhat larger Q^2 and f values in Tables IV and V of III, and the empirical factor to correct them would have been about 0.21 instead of 0.25.]

A further element of uncertainty lies in the ν_{NV} values taken from Table V of III; although the $N \rightarrow V_1$ frequency is empirical, the $N \rightarrow V_2$ and so on frequencies are based on a use of the rough theory. (Even the $N \rightarrow V_1$ frequency is a little uncertain when applied to other molecules than those for which it is spectroscopically known to fit.) Still another uncertainty arises from possible errors in assuming that the Lorenz-Lorentz Eq. (1) is accurate for liquids; W. Hückel states, however,[5] that M obtained from Eq. (1) usually differs only a little for a liquid and its vapor. Finally, there is surely in general some error in attributing the exaltation of the refractivity exclusively to the unsaturation electrons; in this connection it is worth noting that the "normal" double bond refractivity is based on averages over a number of compounds which show quite appreciable positive and negative deviations from the normal formula, that is from Eq. (2) without E.

In spite of all this, the calculations appear adequate to establish the importance of $N \rightarrow V$ transitions for the unsaturation electron contribution to molecular refractivity; and to throw a true light on the general effect of conjugation on refractivity.

By analogy with these results on the unsaturation electrons and on the basis of other results in II,[12] we can further conclude that transitions of the $N \rightarrow V$ type must make considerable contributions to the refractivities of the C−C and C−H bonds, i.e., of the non-"unsaturation" electrons. That the partial refractivities for these are smaller than for the unsaturation electrons (cf. Eq. (2)) is doubtless because the $N \rightarrow V$ transitions come at very considerably higher frequencies for the non-unsaturation than for the unsaturation electrons.[13]

[12] R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939); II of this series.

5. Cyclic Dienes and Benzene. Further Critical Discussion

Referring again to Table IV, we note that among the cyclic dienes (which are necessarily *cis*) the "experimental" refractivity increases in the theoretically predicted manner with angle θ, but is always lower than for *trans* compounds, as predicted. However, the experimental refractivities are definitely lower even than those calculated for *cis* compounds. A possible explanation for this is at hand in the discussion in IV of this series, where we found (both theoretically, and experimentally from the absorption spectra) that the longer wave-length $N \rightarrow V$ transitions have smaller f values than expected for noncyclic *cis* dienes, *most* of the $N \rightarrow V$ f strength (at least in cyclopentadiene) being shifted toward shorter wave-lengths. The matter should, however, be examined quantitatively and in more detail.

Returning again to Table IV, let us consider benzene and its methyl derivatives. Here the number of unsaturation electrons is six. We may try to estimate the f value for the $N \rightarrow V$ transition by multiplying the semi-theoretical value 2.37 for benzene (cf. V, Eq. (13)) by the same factor 0.25 which gave good results for the noncyclic dienes.

With this correction factor 0.25, $f(N \rightarrow V)$ becomes 0.59. Subtracting this from the total number 6 of unsaturation electrons, we get an estimate of 5.41 effective dispersion electrons of the unsaturation type *not* associated with $N \rightarrow V$. Taking 1.25×10^5 cm^{-1} as a mean effective ν for these, as above, and using Eq. (1), we arrive at a deduction of 6.35 to be subtracted from the "experimental" unsaturation electron contribution to M_D, which is 8.65 for benzene (cf. Table I). The balance ascribable to $N \rightarrow V$ is 2.30 for benzene (cf. Table IV), and somewhat larger for the methylated benzenes.

On the other hand, the "calculated" value of Table IV, using $\nu_{NV} = 56{,}000$ and $f(N \rightarrow V) = 0.59$,

[13] Cf. the writer's previously expressed opinion (J. Chem. Phys. **3**, 522 (1935)—second paragraph in second column) according to which the transition $[\sigma+\sigma] \rightarrow [\sigma-\sigma]$ in C_2H_6, which would represent $N \rightarrow V$ for the C−C bond in that molecule, comes at a rather high frequency (certainly not lower than 74,000 cm^{-1}, and probably higher).

is 3.73. The poorness of the agreement indicates that a lower correction factor for the semi-theoretical f, or more probably a higher mean effective frequency ν_{ef} for the non-($N \rightarrow V$) unsaturation-electron transitions, or both, should be used for benzene than for the dienes. As a matter of fact, it is entirely possible that the f correction factor for the dienes (which was based on rough calculations from absorption data) and the ν_{ef} for the dienes, may be considerably in error. It would indeed not be surprising if the f correction factor or especially ν_{ef} would be found to *vary* somewhat, even among the conjugated dienes, with the shape of the molecule. It is also not unlikely that the proper f correction factors may vary somewhat from one $N \rightarrow V$ transition to another for a single molecule. As we shall see in VII, smaller and smaller correction factors on the semi-theoretical f's for $N \rightarrow V_1$ are needed in conjugated polyenes as the number of double bonds increases. It will of course be desirable to check all these factors and other uncertain parameters by careful new experimental measurements on dienes, polyenes and benzene, thus so to speak establishing an empirical calibration of the rough theory. Eventually, refinement of the theoretical calculations will also be expected.

6. Hyperconjugation and Refractivity in Substituted Benzene and Dienes

In conclusion, we may consider the effects of alkyl substitution on the refractivity of benzene, and of butadiene. In the methyl derivatives of benzene, the refractivity increases steadily as methyl groups are substituted. According to W. Hückel's tables,[4] the exaltations E of M_D are as follows: benzene, -0.17; toluene, $+0.14$; *o*-xylene, $+0.23$; *m*-xylene, $+0.36$; *p*-xylene, $+0.48$; mesitylene, $+0.60$. The absorption spectra[14] also show interesting changes,—in general, a shift toward longer wave-lengths paralleling the course of the exaltations. These progressive shifts in the absorption spectra (in particular, in the $N \rightarrow V$ spectrum) with methylation are qualitatively able to explain the increasing exaltation, and rough calculations indicate that the observed changes are also quantitatively of the right order of magnitude.

As a constitutional cause of these absorption spectrum shifts and the increasing exaltation, we may not unreasonably look to the phenomenon of hyperconjugation discussed in IV of this series.[2] Each methyl group substituted in a benzene ring brings with it six C−H bonding electrons, two of which, in MO approximation, occupy an MO which is antisymmetrical to the plane of the ring and so must interact more or less with the unsaturation-electron MO's of the ring. This hyperconjugation is thus analogous to the conjugation which occurs in the styrols, where the group $-CH=CH_2$ instead of $-C\equiv H_3$ as here is substituted in the ring (compare the discussion of cyclopentadiene in Section 1 of IV, in particular the analogy of hyperconjugation with $-C=H_2$ there to conjugation with $-C=CH_2$ in fulvene). Hyperconjugation of methyl groups with the mobile electrons of the benzene ring is very similar to hyperconjugation in the methyl-substituted ethylenes (cf. IV, Section 7), and like the latter is the presumably relatively strong *first-order* hyperconjugation (cf. IV, Section 8). In both cases it seems capable (as also in the cyclic dienes) of explaining the shift of absorption bands toward longer wave-lengths.

Particularly striking in the methyl-substituted benzenes is the steady increase in the exaltation with increase in the number of substituted methyl groups. Also of interest is the increasing exaltation with increasingly symmetrical distribution of the methyl groups in the xylenes. Although in other cases, e.g. the substituted butadienes, pronounced changes in exaltation on methylation might be explainable in terms of changes in shape of the molecule skeleton, this is hardly possible in the case of the methylated benzenes, especially when we consider the more symmetrical ones, particularly mesitylene (symmetrical trimethylbenzene). Thus hyperconjugation is indicated with unusual clarity as the cause; and as a cause of effects of quite appreciable size.

Let us now return to the open-chain substituted butadienes in Table IV. Liquid butadiene itself is known fairly conclusively from Raman data to be pure *trans* (cf. III). As compared with butadiene itself (for which, however, the data are

[14] Cf. *e.g. International Critical Tables*, Vol. V, p. 361, Figs. 1, 2, 4.

not very accurate) the substituted butadienes fall into two groups. The centrally-substituted butadienes (β-methyl- and β,γ-dimethylbutadiene) have considerably lower refractivities than butadiene itself. This might plausibly be accounted for (cf. discussion in III) by supposing that these substances exist as mixtures of cis- and trans-forms,—or that β,γ-dimethylbutadiene in the liquid state is nearly all *cis*. Against this explanation, however, objections may be raised: (1) there seems to be no "steric" or other obvious reason why central substitution rather than end substitution should induce a *cis* arrangement; (2) the explanation does not account for the observed progressively increasing exaltation with increasing end-substitution (or decreasing central-substitution).

Quite possibly hyperconjugation may be able alone to account for the decreased exaltation in the case of centrally-substituted methyl groups. This is suggested rather definitely by refractivity data on the methyl-substituted styrols,[4] where an explanation in terms of cis-forms or of changes in θ seems hardly possible. Decrease of exaltation by hyperconjugation in the foregoing examples might well be explainable by the *cis*-like orientation of the CH_3 groups relative to the double bonds with which they are hyperconjugated. The matter should be studied further.

The end-substituted butadienes (1,3-pentadiene or 1-methylbutadiene, 2,4-hexadiene or 1,4-dimethylbutadiene, and 2,4-heptadiene or 1-methyl-4-ethylbutadiene), where it is likely that all or most of the carbon atoms are strung out in a *trans-trans-trans* . . . arrangement, show increasingly large exaltations. This may probably be explained by hyperconjugation. As in the substituted benzenes, so again here we note that the effects attributed to hyperconjugation are of quite respectable size. Hyperconjugation with end-substituted methyl groups is somewhat analogous to ordinary conjugation in a higher polyene; for example, 2,4-hexadiene ($H_3{\equiv}C-CH=CH-CH=CH-C{\equiv}H_3$) may be compared with octatetraene ($H_2C=CH-CH=CH-CH=CH-C=CH_2$).

From the foregoing discussion it seems that hyperconjugation may be an important element in determining exaltations in alkyl-substituted butadienes, benzenes, and styrols. If so, our attribution to the unsaturation electrons exclusively of the exaltation in Tables I, IV ("experimental" column), and elsewhere is not wholly correct. That part of the exaltation which is due to hyperconjugation should be ascribed jointly to the double-bond unsaturation electrons and to the quasi-unsaturation electrons of the alkyl groups which enter into hyperconjugation.

All in all, the present investigation of the theoretical explanation of refractivity data is of value probably as much for the possibilities it discloses for future work[15] as for the definite results which it yields. In conclusion, the writer wishes to express appreciation to Dr. G. W. Wheland for helpful discussions and references.

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[15] In this connection, Dr. G. Egloff's *Physical Constants of Hydrocarbons*, in four volumes (Reinhold Publishing Co., 1939–40) will be a valuable reference source. The writer is indebted to Dr. G. Egloff, Dr. R. B. Dull, and Dr. J. Sherman of the Universal Oil Products Co. for data from this source, used in Tables I and IV.

Intensities of Electronic Transitions in Molecular Spectra

VII. Conjugated Polyenes and Carotenoids

ROBERT S. MULLIKEN
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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The observed absorption spectra of conjugated polyenes and their derivatives are compared with the results of theoretical calculations on various models of butadiene, octatetraene, and β-carotene. In each case the unsaturation electrons give rise to a series of $N\rightarrow V$ electronic transitions which spread over an increasing range of the spectrum with increase in the number of conjugated double bonds. According to the theory, the greater part of the whole $N\rightarrow V$ intensity is concentrated in its longest wave-length member $N\rightarrow V_1$, and the latter gets more and more intense as it shifts toward longer wave-lengths with increase in the number of conjugated double bonds. Exactly this behavior has been observed experimentally in the spectra of the conjugated polyenes and their derivatives. Thus we obtain a satisfactory theoretical explanation of the existence of strong color in polyene pigments and related compounds, i.e. in the carotenoids. Quantitatively, the theory (when the rough Hückel molecular orbital approximation is used) requires empirical adjustment or calibration; new experimental work on the spectra of the lower polyenes would be valuable in this connection. The relations between absorption and fluorescence spectra ($N\rightarrow V_1$ and $V_1\rightarrow N$) in the substituted polyenes are discussed. An explanation is given of the "gap" between the longest wave-length absorption band and the shortest wave-length fluorescence band.

According to the theory, the shape of the molecule strongly affects the distribution of intensity and somewhat affects the total intensity in the $N\rightarrow V$ spectrum. The more elongated the molecule, the greater the total intensity, and the greater the preponderance of intensity in the longest wave-length transition $N\rightarrow V_1$. The α-furyl polyene aldehydes and acids may be cited as affording probable illustrations of this effect. Here the introduction of the furyl group, although it contains two conjugated double bonds, increases the $N\rightarrow V_1$ intensity much less than if the same grouping $-HC=CH-CH=CH-$ had been added to the polyene chain. The explanation given here is that the two double bonds increase the over-all length of the molecule much less when they are bent around as in the furyl ring than when they are stretched out in a zigzag chain as apparently they are in the simple polyenes and polyene aldehydes and acids. According to the theory, the $N\rightarrow V_1$ transitions in conjugated polyenes and their derivatives are polarized approximately along the long axis of the molecule. This should give rise to a high polarizability of such molecules along that direction, which may help explain their reactivity, in particular their tendency to polymerize.

1. INTRODUCTION

AN extension of the discussion[1] of the spectra of open-chain conjugated dienes to those of conjugated polyenes and their derivatives offers interesting possibilities. The extensive measurements of Smakula, Kuhn, Hausser, and associates[2, 3] on the spectra of polyene aldehydes, polyene acids, diphenylpolyenes, and the carotenoids furnish much valuable material for comparison with theory. Data are also available for vitamin A, which is a simple derivative of decapentaene.[3a] Although among these only some of the carotenoids[3a] are pure polyenes, the measurements indicate that the polyene part of the molecule has a predominant influence for the long wave-length part of the spectrum of nearly all the molecules mentioned.

In all of them, one very strong absorption transition, usually with a definite characteristic vibrational structure pattern, is observed. Other transitions at shorter wave-lengths are found but are much weaker. In all, the strong transition shifts progressively toward longer wave-lengths with increase in the number of conjugated double bonds; but the rate of shift becomes smaller and smaller as the polyene chain gets longer. From about eight double bonds on, the absorption peak lies in the visible. The height of this peak and the total area under it (proportional to the f value) increase linearly with the number n of conjugated double bonds, at least for the smaller n values. For beta-carotene

[1] R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939): III of this series.
[2] K. W. Hausser, Zeits. f. tech. Physik **15**, 10 (1934). A. Smakula, Zeits. f. angew. Chemie **47**, 657 (1934).
[3] K. W. Hausser, R. Kuhn, and others, Zeits. f. physik. Chemie **29B**, 364 *et seq.* (1935).
[3a] Cf. *e.g.* H. Gilman, *Organic Chemistry* (John Wiley & Sons, 1938).

($n=11$) and similar molecules, the f value for the transition (after allowing for the effect of the solvent, see below) is about 1.5.

As we shall now see from a survey of the theoretical possibilities, it is entirely probable that the characteristic strong absorption peak just considered is in all cases due to an $N\rightarrow V$ transition analogous to $N\rightarrow V_1$ of the conjugated dienes already discussed. From our survey of the theory, it will appear that the observed transition is the longest wave-length one of a number of $N\rightarrow V$ transitions (say $N\rightarrow V_1$, $N\rightarrow V_2$, $N\rightarrow V_3$, and so on) scattered through the spectrum, all the others being much weaker. The concentration of the major part of the intensity of the several $N\rightarrow V$ transitions in their longest wave-length member is entirely analogous to what we have already found in transbutadiene (cf. Tables IV, V of III), and may now be taken as a characteristic effect of conjugation established both theoretically and experimentally.

Theoretical intensity calculations can be made for the higher conjugated polyenes following the same general procedures as were used above for the conjugated dienes. In the present paper, calculations will be made only for octatetraene ($n=4$) and for beta-carotene ($n=11$), since a consideration of these molecules together with the dienes ($n=2$) will suffice to establish with reasonable certainty the conclusions stated above. More systematic and thorough calculations can be left until later.

2. Octatetraene

In octatetraene there are eight unsaturation electrons, corresponding to which there are eight unsaturation electron MO's (say χ_1, χ_2, $\cdots\chi_8$). In the normal state the first four of these are occupied, each by two electrons. The energies and forms of the eight MO's can be worked out along the same lines as were used for "case II" of 1, 3-butadiene (cf. Table II of III). However, the Hückel approximation instead of the Lennard-Jones approximation will be used here, since it is simpler. The difference is not very great, even for 1, 3-butadiene (cf. Table II of III, note 2), and in octatetraene it is less.

If we let

$$\chi_i=a_i\phi_1+b_i\phi_2+\cdots h_i\phi_8, \qquad (1)$$

where the ϕ's refer to $2p_x$ carbon orbitals of the eight carbon atoms, the eight χ's and their relative energies in the Hückel MO approximation are as given in Table I. Assuming that the molecule is plane, they are otherwise independent of its form.

Three plausible forms for the skeleton of octatetraene are shown in Fig. 1. Form I is analogous to the trans-form of 1, 3-butadiene, and is presumably the actual form, since the same forces which make the trans-form the actual one in butadiene (cf. III) should operate here to favor form I. Form II and especially III are partly like the cis-form of butadiene. Forms still more closely analogous to cisbutadiene seem to be definitely excluded for steric reasons (too close approach of H atoms), assuming that the molecule remains plane. Thus it appears that even the most compact or cis-like forms which could be considered for octatetraene or its derivatives have a rather extended structure, more like *trans* than like *cis*. This should be reflected in the spectra. Similar remarks are applicable, in varying degrees, to the higher polyenes.

For each of the two forms I and III of Fig. 1, intensities of all the possible $N\rightarrow V$ transitions have been calculated, assuming all bond angles to be 120°. Details of the calculations are analogous to those given in III for 1, 3-butadiene, and need not be included here. The results are recorded in Table II.

Table I. *Forms and energies of LCAO MO's of normal octatetraene (Hückel approximation).*[1]

Name of MO	Coefficients in Eq. (1)[2]								Relative Energy[3]
	a_i	b_i	c_i	d_i	e_i	f_i	g_i	h_i	
χ_1	t	u	v	w	w	v	u	t	-1.879ϵ
χ_2	u	w	v	t	$-t$	$-v$	$-w$	$-u$	-1.532ϵ
χ_3	v	v	0	$-v$	$-v$	0	v	v	-1.000ϵ
χ_4	w	t	$-v$	$-u$	u	v	$-t$	$-w$	-0.347ϵ
χ_5	w	$-t$	$-v$	u	u	$-v$	$-t$	w	0.347ϵ
χ_6	v	$-v$	0	v	$-v$	0	v	$-v$	1.000ϵ
χ_7	u	$-w$	v	$-t$	$-t$	v	$-w$	u	1.532ϵ
χ_8	t	$-u$	v	$-w$	w	$-v$	u	$-t$	1.879ϵ

[1] All the results given in Table I are obtained from equations identical with Eqs. (2) and (3) below, except that the numbers 22 and 23 in those equations are here replaced by 8 and 9.

[2] In Hückel's approximation, if we neglect overlapping integrals as in Table II of III, we have $t=0.161$, $u=0.303$, $v=0.409$, $w=0.464$. Hückel's approximation assumes all bond-distances equal.

[3] The energies[5] are given by an additive constant plus the multiple of ϵ indicated in the Table; $-\epsilon$ is the value of the resonance integral (Hückel's β) evaluated for a C−C distance equal to the average of the shorter and longer bond-distances in the molecule, i.e., about 1.39A (cf. Table II, note 4).

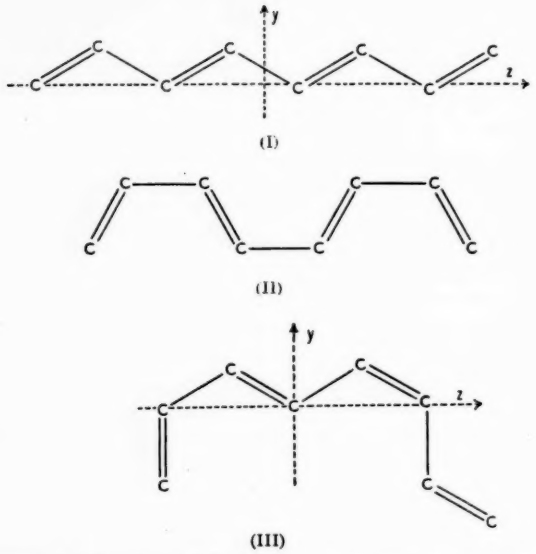


FIG. 1. Conceivable forms of octatetraene. The y and z axes shown were chosen for convenience in the subsequent intensity calculations.

Table II shows the same kind of relations as does Table IV of III for 1,3-butadiene with $\theta=30°$. The greatest total Q^2 is found for form I, which is the most extended (trans-like) form possible for octatetraene. Moreover, the concentration of the intensity in the longest wavelength transition "$N\rightarrow V_1$" is most complete for form I. Even in form I, however, a small amount of intensity is scattered in a series of weak transitions of the $N\rightarrow V$ group over a wide range of the spectrum. The total range covered is considerably extended toward longer and (still more) toward shorter wave-lengths, as compared with 1,3-butadiene. The intensity center of gravity, however, is shifted toward longer wavelengths. The calculated intensity per molecule in the longest wave-length transition (and in the sum of all the transitions) is greatly increased as compared with 1,3-butadiene.

The polarization relations shown by Table II are also interesting, and show similarities to those for butadiene. In the strong transition $N\rightarrow V_1$, the direction of polarization is approximately that of the long axis of the molecule. Most of the other, weaker, transitions, however, are polarized approximately perpendicularly to this axis. In all cases, the electric vector vibrates in the plane of the molecule.

Comparing Table II here with Table IV of III, the quantity Q^2 for $N\rightarrow V_1$ is seen to be multiplied by approximately four. The absorption intensity, however, is increased somewhat less when allowance is made for the decreased frequency. If we use the value $\epsilon=15{,}500$ cm^{-1} obtained in Section 5 of III, and the expressions for the respective $N\rightarrow V$ frequencies given in Table IV of III and Table II here, then $N\rightarrow V_1$ should be displaced about $-10{,}000$ cm^{-1} in octatetraene as compared with 1,3-butadiene, and should lie at about 38,000 cm^{-1}. [From Fig. 6 of Hausser's paper,[2] on the other hand, the estimated value is 33,000 cm^{-1}, but it is not clear whether the number of double bonds should be counted the same way for simple polyenes as for the molecules on which this curve is mainly based. In any case, the difference is not very great.]

Using 38,000 cm^{-1} tentatively for the frequency of $N\rightarrow V_1$ in octatetraene, we calculate f for the transition to be 3.92 for form I, 2.34 for form III. An intermediate value is obtained for form II of Fig. 1.

These calculated f values may be compared with the calculated value 1.17 for transbutadiene

TABLE II. *Q^2 and frequency values for $N\rightarrow V$ transitions in octatetraene (Hückel MO approximation), for 120° bond angles.*

TRANSITION[1]	FREQUENCY[2]	Q^2 (form I)[3,4]			Q^2 (form III)[4]		
		Q_y^2	Q_z^2	Q^2	Q_y^2	Q_z^2	Q^2
$N\rightarrow V_1(\chi_4\rightarrow\chi_5)$	$0.69\epsilon+\gamma$	0.24	9.16	9.40	0.17	5.46	5.63
$N\rightarrow V_2(\chi_4\rightarrow\chi_6)$	$1.35\epsilon+\gamma$			0.00*	1.70	0.02	1.72×
$\rightarrow V_3(\chi_3\rightarrow\chi_5)$							
$\rightarrow V_4(\chi_2\rightarrow\chi_5)$	$1.88\epsilon+\gamma$	0.00	0.15	0.15	0.10	0.03	0.13×
$\rightarrow V_5(\chi_4\rightarrow\chi_7)$							
$(\chi_3\rightarrow\chi_6)$	$2.00\epsilon+\gamma$	0.25	0.07	0.32	0.00	0.00	0.00
$(\chi_4\rightarrow\chi_8)$	$2.23\epsilon+\gamma$			0.00*	0.17	0.01	0.18×
$(\chi_1\rightarrow\chi_5)$							
$\chi_3\rightarrow\chi_7$	$2.53\epsilon+\gamma$			0.00*	0.05	0.21	0.26×
$\chi_2\rightarrow\chi_6$							
$\chi_3\rightarrow\chi_8$	$2.88\epsilon+\gamma$	0.00	0.01	0.01	0.29	0.00	0.29
$\chi_1\rightarrow\chi_6$							
$\chi_2\rightarrow\chi_7$	$3.06\epsilon+\gamma$	0.24	0.00	0.25	0.03	0.01	0.04
$\chi_2\rightarrow\chi_8$	$3.41\epsilon+\gamma$			0.00*	0.04	0.12	0.15
$\chi_1\rightarrow\chi_7$							
$\chi_1\rightarrow\chi_8$	$3.76\epsilon+\gamma$	0.25	0.00	0.25	0.05	0.00	0.05
Total		0.98	9.39	10.37	2.60	5.86	8.45

[1] *All* transitions in which *one* electron jumps from an unexcited unsaturation-electron MO(χ_1, χ_2, χ_3, or χ_4) to an excited one (χ_5, χ_6, χ_7, or χ_8) are included. The resulting sixteen $N\rightarrow V$ transitions correspond to the four $N\rightarrow V$ transitions in the dienes.

[2] Based on Table I (cf. Table IV of III and its notes and accompanying discussion). The quantity γ corresponds to $\delta+\eta$ of Table IV of III.

[3] Transitions for which Q^2 is indicated by 0.00* are forbidden for form I.

[4] In the calculations of Q^2, the values $r=1.36$A and $R=1.43$A were taken for the shorter and the longer bonds; these are based on Lennard-Jones' calculations.[4] The results would not have been much different if all bond distances had been assumed equal, as should perhaps have been done for consistency (see Table I, notes). The axes y and z are chosen as in Fig. 1. The y and z components of Q have the *same sign* (or else one of the two components is practically zero), *except* in cases marked with a superscript cross, where Q_y and Q_z have opposite signs.

and 0.53 for cisbutadiene (cf. Table V of III). They should, of course, as we have seen in II and in III of this series, be multiplied by a suitable factor less than one before we can expect them to agree with experiment. For butadiene, this factor was 0.25 using the Lennard-Jones approximation (cf. III), or 0.21 using the Hückel approximation (cf. VI). As we shall see a little later, a somewhat smaller factor is probably needed for octatetraene.

3. Beta-Carotene

Next, as an example of a higher polyene, let us consider β-carotene. A conceivable form ("model II") for the skeleton of this molecule, which contains eleven conjugated double bonds, is given by Fig. 2. As a second among a variety of other conceivable models, we may consider as "model I" an arrangement with maximum elongation for the system of conjugated single and double bonds, i.e., a simple zigzag arrangement as in Fig. 1, model I for octatetraene. For any model, carbon-carbon distances in the conjugated chain should be all nearly equal,[4] with a value of about 1.39A.

For any model, there are 22 unsaturation-electron χ's for the 22 unsaturation electrons. In the Hückel MO approximation,[5] these χ's and their energies E are given by the following equations:

$$\chi_n = C \sum_{f=1}^{22} \sin\,(n\pi f/23)\phi_f, \qquad (2)$$

$$E_n = E_0 - \alpha - 2\epsilon \cos\,(n\pi/23). \qquad (3)$$

Here ϕ_f is the $2p_z$ orbital of the fth carbon atom in the conjugated chain, and C is a normalizing factor which turns out to be $1/3.38$ for all the χ's if overlapping integrals are neglected. E_0 is the energy for a $2p_z$ orbital in an isolated carbon atom, α a Coulomb integral, and ϵ a resonance integral.

After setting up electron configurations for N and V states, we can calculate Q^2 values for the various $N \rightarrow V$ transitions in the usual way. It will suffice for the present to give, in Table III, results of such calculations on just a few of the longest wave-length $N \rightarrow V$ transitions.

[4] Cf. references 8, 14 of III of this series.

[5] E. Hückel, Zeits. f. Physik **70**, 241–2 (1931); **76**, 635–6 (1932); Zeits. f. Elektrochem. **43**, 782 (1937).

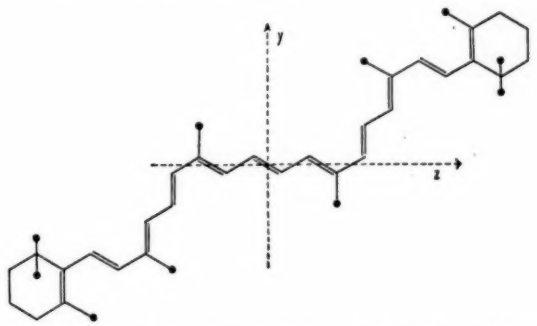


Fig. 2. Carbon skeleton for a possible model (model II) of β-carotene. Each of the dots represents a methyl group. Elsewhere, hydrogens are attached to the carbons. The axes y and z were chosen for convenience in the subsequent intensity calculations.

Table III shows the same kind of relations as Table II for octatetraene: the longest wave-length transition $N \rightarrow V_1$ is by far the strongest, and most so for the most elongated model (model I). Further, the transition $N \rightarrow V_1$ is polarized approximately along the long axis of the molecule. Presumably the numerous shorter wave-length $N \rightarrow V$ transitions not given in Table III would all be very weak.

A comparison with the observed spectrum of β-carotene is now of interest. Smakula[2] and Hausser[2] give quantitative absorption curves for α-carotene, β-carotene, and various carotenoids[3a] in hexane solution, those of Smakula extending to λ2000.[6] The strong absorption region which we identify as $N \rightarrow V_1$ extends from about λ5100 to λ3600 for β-carotene, a range of about 8200 cm^{-1}. This over-all width is about the same as for $N \rightarrow V_1$ in other polyenes and substituted polyenes; for example, in butadiene this width is about 10,000 cm^{-1}. The $N \rightarrow V_1$ absorption shows some vibrational structure,[3] with its highest peak at about $\nu = 22{,}400$. A similar structure is found in other polyenes and their derivatives. After the $N \rightarrow V_1$ region, the absorption falls gradually to a moderately deep minimum near λ3100, then rises to a peak at about λ2744 ($\nu = 36{,}400$). This is about a sixth as high as the main peak. After another minimum near λ2300, the absorption begins rising again.

These observations, so far as they go, agree in a general way with the predictions of Table III.

[6] R. Pummerer and L. Rebmann, Ber. Chem. Ges. **61**, 1099 (1928), also give a quantitative absorption curve, for "carotene."

However, the second peak is stronger than we would expect for models I and II. Possible explanations are: (A) the actual molecule may be much less elongated (more like cisbutadiene) than models I and II; this would direct more of the intensity into the shorter wave-length $N \rightarrow V$ transitions, if we may judge by analogy with butadiene and octatetraene; (B) the absorption peak at λ2744 might be due to a Rydberg series transition; (C) it may be that the approximation we are using underestimates the relative intensities of the higher frequency $N \rightarrow V$ transitions.

Of special interest is a comparison between observed and calculated strength for the $N \rightarrow V_1$ transition. By the methods described in Table VI of III, footnote 4, an f value of 1.52 electrons is obtained experimentally from Smakula's data.

The semi-theoretical f falue for models I and II, using $\nu_{max} \approx 0.22 \times 10^5$ cm^{-1} and $Q^2 = 45.6$ or 66.8 (cf. Table III), comes out 11.0 or 16.1 electrons. From general theoretical considerations, such values are obviously much too large, since the value 2.00 is a theoretical upper limit for any one spectroscopic transition in a system where there is no degeneracy. Specifically, our $N \rightarrow V_1$ transition depends on exciting an electron out of the group or shell of two electrons which in the normal state of the molecule occupy the χ_{11} molecular orbital. By the usual f sum rule, the sum of the f's for *all* transitions in which one or both electrons are excited out of this shell is just two.

Thus it is seen by *general* theoretical considerations that the empirical ν combined with the Hückel LCAO MO Q^2 gives much too large a semi-theoretical f here. The latter is thus seen to be more in error for higher polyenes than for smaller molecules such as ethylene and butadiene. The error can be expressed by finding the empirical correction factor needed to bring the semi-theoretical f down to the observed. This factor was found in II to be about 1/3 for O_2, and in III to be probably about 0.25 for conjugated dienes. Here the factor is about $(1.52/11.0) = 0.14$ or $(1.52/16.1) = 0.09$ according as we assume model II (cf. Fig. 2) or model I.

Whether model I or model II or some other represents β-carotene in solution cannot be definitely stated on the basis of the evidence given here. However, it seems probable from the evidence discussed in III and VI that the most elongated possible model (model I) is correct. The work[7] of Kuhn and Winterstein and of Kuhn and Hoffer on certain carotenoids and methyl polyene acids shows that *cis* and *trans* isomers can be isolated when a group COOR is present at the end of a conjugated polyene chain

(thus: HC=CR−CH=CH−C(=O)−).

It seems then that the conjugation of C=C and C=O gives isomers sufficiently stable to be isolated, but that the polyene chain probably exists only in one form (if so, in all probability the trans-form), or possibly exists in several forms which are labile.

Table III. *Values of frequency and Q^2 calculated for $N \rightarrow V$ transitions in β-carotene (Hückel MO approximation).*

Transition	Frequency[1]	Q^2 (Model II, Fig. 2)[3]			Q^2 (Model I)[3]		
		Q_y^2	Q_z^2	Q^2	Q_y^2	Q_z^2	Q^2
$N \rightarrow V_1$ ($\chi_{11} \rightarrow \chi_{12}$)	$0.272\epsilon + \delta + \eta$	9.95	35.6	45.6	0.24	66.6	66.8
$N \rightarrow V_2$ ($\chi_{10} \rightarrow \chi_{12}$)	$0.545\epsilon + \delta + \eta$			0.00[2]			0.00[2]
$N \rightarrow V_3$ ($\chi_{11} \rightarrow \chi_{13}$)							
$N \rightarrow V_4$ ($\chi_9 \rightarrow \chi_{12}$)	$0.804\epsilon + \delta + \eta$	1.82	0.15	1.97	and so on		
$N \rightarrow V_5$ ($\chi_{11} \rightarrow \chi_{14}$)							
$N \rightarrow V_6$ ($\chi_{10} \rightarrow \chi_{13}$) and so on	$0.818\epsilon + \delta + \eta$ etc.	0.60	0.01 etc.	0.61			

[1] The frequencies are calculated on the basis of the χ energies of Eq. (3), adding a quantity $\delta + \eta$ to allow for electronic interactions as explained in III of this series, Table IV, note 2.
[2] These transitions are forbidden by selection rules for both models.
[3] The y and z axes for model II are as shown in Fig. 2. For model I (pure *trans* arrangement) the z axis crosses every one of the C=C and C−C conjugated bonds at its mid-point, if all bond-lengths are assumed equal.

4. Energy Levels, Absorption Spectra, Polarizability, and Chemical Reactivity in Conjugated Polyenes

We are now in a position to make some generalizations. In the first place, the data just cited and numerous other data of similar nature on polyene pigments and on substituted polyenes,[2, 3] in connection with our theoretical calculations, make it extremely probable that the very strong long wave-length absorption maximum observed in all is our $N \rightarrow V_1$ transition. Although the theory fails badly in a quantitative sense, it predicts qualitatively correctly the shift toward longer wave-lengths, with steadily increasing always high intensity, of the $N \rightarrow V_1$ transition with increase in number of conjugated double

[7] R. Kuhn and A. Winterstein, Ber. **65**, 646 (1932); **66**, 212 (1933). R. Kuhn and M. Hoffer, Ber. **65**, 651 (1932).

bonds. It gives us thus a very definite explanation of the cause of color in the carotenoids.

It also gives us a good idea of the nature of the excited energy levels of such molecules. Although color is due mainly to a single transition to the *lowest* excited *singlet* electronic state, there should probably be at least one, perhaps several, triplet states of lower energy, as well as a long series of singlet and triplet states of higher energy. All these triplet and higher singlet states should be spectroscopically inconspicuous but might be of some importance for chemical reactions. Hückel[8] has already discussed the correlation of chemical activity with the positions of excited electronic states as calculated by him. The present work makes this somewhat more definite by empirically locating the lowest excited singlet state in polyenes and their derivatives,—showing, incidentally, that it is not as low as one might think from Hückel's calculations.

From the available data on the carotenoids and other substituted polyenes,[2, 3] it looks as if the frequency of the $N \rightarrow V_1$ transition approaches a limiting value as the number n of conjugated double bonds increases. From our discussion in Section 3, it also appears probable that the f value of this transition approaches a limiting value 2. We may ask, what would the approach of the frequency of $N \rightarrow V_1$ to a limiting value mean? Theoretically, the heights of the states V_1 and T_1 above N (the energy interval N to V_1 being equal to h times the frequency just discussed), should be given (cf. Table III, note 1) by

$$E_n(V_1, T_1) = \rho_n \epsilon \pm \delta + \eta, \qquad (4)$$

where the upper sign is for V_1, the lower for T_1; ρ_n approaches zero as $n \rightarrow \infty$, according to the theory.[5]

If the frequency of $N \rightarrow V_1$ approaches a constant value as $n \rightarrow \infty$, this must be equal to $\delta + \eta$. [Of course δ and η themselves may also vary with n, but presumably only slowly for large n.] There seem to be two possibilities: (A) δ remains finite as $n \rightarrow \infty$; (B) $\delta \rightarrow 0$ as $n \rightarrow \infty$. In case (A) the singlet-triplet interval would approach a finite limiting value, in (B) a limiting value zero. In case (A), there would seem to be a possibility that, beyond some value of n, state T_1 would be below state N, so that the substance would be paramagnetic. In case (B), the limiting value of E for both V_1 and T_1 would be η.

It seems likely that case (B) is the actual case, since the quantity δ represents an interaction integral between two electrons in two different MO's. This should decrease if the average distance between the electrons in the two MO's increases with increasing n. Since the two MO's in question both extend throughout the whole system of conjugated double bonds, the chances for the two electrons (one in each MO) to be far away from each other do increase at the expense of the chances for their being near each other as n increases. Hence probably δ does approach zero as n increases. However, the matter should be examined more rigorously.

If low excited electronic states are directly involved in reaction mechanisms, the foregoing argument tends to show that, while the T states require considerably less activation energy than the V states in the lower polyenes, in the higher polyenes this difference decreases.

Some other considerations which may have a bearing on chemical reactivity are of interest. Let us consider the calculated Q values of Tables II and III for the $N \rightarrow V_1$ transition, taking in each case the value for the most extended (all-trans) form of the molecule; and let us compare these with the maximum linear dimension L of the system of conjugated double bonds in the molecule. For octatetraene we find $Q = (9.40)^{\frac{1}{2}} = 3.07$A as compared with $L = 8.45$A; for β-carotene $Q = (66.8)^{\frac{1}{2}} = 8.17$A, compared with $L = 25.3$A. Thus for octatetraene, $Q(N \rightarrow V_1) = 0.36L$ and for β-carotene $Q(N \rightarrow V_1) = 0.32L$. These results may be compared with those for diatomic molecules and for ethylene (cf. II of this series), where $Q(N \rightarrow V) = L/2^{\frac{1}{2}} = 0.71L$. Interpreted in terms of an effective oscillating charge, it is as if a considerable fraction of an electronic charge oscillated back and forth along the whole length of the chain of conjugated double bonds. This indicates that the state V_1 in the polyenes has pronounced ionic character (like V in ethylene), with a considerable probability of opposite charges occurring on or near the two ends of the chain. [The AO wave function of state V_1 then doubtless represents a superposi-

[8] E. Hückel, Zeits. f. Physik **76**, 640–641 (1932).

tion of many varied ionic states, but the high intensity of the transition $N \rightarrow V_1$ is presumably connected with a strong predominance in V_1 of wave functions with charges widely separated, including two wave functions with a plus charge at one end and a minus at the other end of the chain.]

In view of the well-known relations between polarizability, refractivity, and absorption spectra (in this connection, cf. VI of this series), the high intensity and low frequency of $N \rightarrow V_1$ in the polyenes imply high polarizability for these molecules. Further, this polarizability should be especially high *along the length of the chain*, since the dominant transition $N \rightarrow V_1$ is polarized approximately along that direction (cf. Tables II, III). Hence polyene molecules should be especially sensitive to polarization lengthwise and at their ends. This is presumably connected with their reactivity, in particular with their tendency to polymerize, and with the tendency for the *end* carbon atoms of a polyene chain in substituted polyenes to add hydrogen atoms on hydrogenation.[7, 8]

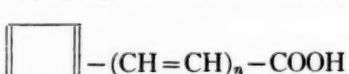
All this applies, of course, assuming the molecules to have highly elongated (pure trans) forms. Molecules which for any reason may be more cis-like should have weaker $N \rightarrow V_1$ spectra, smaller and less predominantly longitudinal polarizability, and lower reactivity. The stabilizing effect (as regards reactivity) of rings at the ends of a polyene chain, as for example in the diphenylpolyenes, is presumably connected with this.

5. Substituted Conjugated Polyenes

Although our discussion so far has been concerned with conjugated aliphatic polyenes, that is with pure aliphatic hydrocarbon molecules containing conjugated double bonds, it is more or less applicable also to various derivatives of these, such as the diphenylpolyenes, polyene aldehydes and acids, and the furyl-polyene aldehydes and acids, on all of which extensive measurements have been made.[2, 3] In these molecules, phenyl, C=O, or furyl groups enter into conjugation with the double bonds of the polyene chain. We shall not here attempt any theoretical consideration of such substituted polyenes beyond a few remarks.

Experimentally it seems clear[2, 3] that the unsaturated groups just mentioned have essentially the same effect for the long wave-length spectrum as C=C groups. In the case of C=O groups, it may be that the two C=O bond unsaturation electrons behave nearly like C=C unsaturation electrons in interacting with the latter. From the observed spectra it appears that in all cases there is a very intense $N \rightarrow V_1$ transition which becomes more intense and progresses steadily toward longer wave-lengths with increase in the length of the polyene chain. Toward shorter wave-lengths, much weaker absorption regions are generally observed at first, until finally we come to intense absorption regions characteristic of the substituent groups.

The α-furyl polyene acids and aldehydes



and

show effects which can be explained in an interesting way. As compared with the corresponding methyl polyene acids and aldehydes

$$CH_3-(CH=CH)_n-COOH$$

and

$$CH_3-(CH=CH)_n-CHO,$$

the replacement of the methyl group by the furan ring has exactly the same effect on the $N \rightarrow V_1$ *frequency* as if *two conjugated double bonds* had been added.[2, 3] This is exactly what might be expected provided hyperconjugation by the O atom (cf. IV of this series) has no appreciable effect on the frequency. This seems to be at least not seriously inconsistent with what is known about the spectrum of furan itself (cf. IV).

The interesting point, however, is that the $N \rightarrow V_1$ *intensity* is increased, by substitution of for CH_3, much *less* than if n, the number of ordinary polyene double bonds, had been increased by two; in fact, the increase in intensity

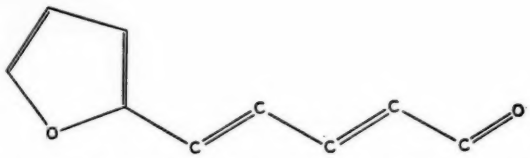


FIG. 3. Carbon, oxygen skeleton of α-furyl 1,3-pentadiene aldehyde.

is somewhat less than if n had been increased by *one*. [The smallness of the increase in intensity is also confirmed by a relatively low molecular refractivity.] A simple explanation can be given if the polyene chain and its attached C=O group in the polyene acid and aldehyde molecules have the elongated configuration shown in Fig. 3. Such a configuration is analogous to the *trans* arrangement in 1,3-butadiene, and such a configuration gives theoretically the maximum possible intensity to $N \rightarrow V_1$, as we have seen in III and in the present paper.

This applies to the polyene chain and its attached >C=O group in Fig. 3. But the two double bonds in the furyl group in Fig. 3, because of the ring structure, give not nearly as much further elongation of the whole molecule as if n in the polyene chain had been increased by two. The compactness of the furyl group, combined with an elongated arrangement of the rest of the molecule, seems capable of explaining the relative ineffectiveness of the furyl double bonds in increasing the $N \rightarrow V_1$ absorption intensity.

An interesting feature noted by Hausser, Smakula, and co-workers[2, 3] in their work on the substituted polyenes is that the height and the f value of the $N \rightarrow V_1$ absorption peak increase linearly with the number of conjugated double bonds. This is in at least rough agreement with our theoretical calculations on the polyenes. However, as was pointed out in an earlier paragraph, the f value for $N \rightarrow V_1$ cannot possibly exceed 2 as an upper limit; hence the linear increase just mentioned cannot continue indefinitely. The observed linear behavior was for molecules with at most a rather small number of double bonds.

6. Absorption and Fluorescence in Substituted Conjugated Polyenes

A puzzling phenomenon reported by Kuhn, Hausser, and co-workers in their comparative study of absorption and fluorescence in polyene derivatives is the existence of a gap between the longest wave-length absorption band in the vibrational structure of $N \rightarrow V_1$ and the shortest wave-length band in the corresponding $V_1 \rightarrow N$ fluorescence spectrum. It is worth noting, however, that there seems to be still a small amount of absorption and emission at the middle of the gap.[9] The width of the gap increases with increase in the number of conjugated double bonds. The absorption and fluorescence spectra are roughly mirror images of each other on a frequency scale.[2, 3, 9] There seems to be no reason, especially in view of our theoretical analysis, to doubt that the fluorescence spectrum really is $V_1 \rightarrow N$. According to the theory, no other excited singlet level should be below V_1. Fluorescence from a triplet level lying below V_1 would be possible, but for various obvious reasons this should be weak; besides, the gap mentioned above is hardly wide enough to correspond to a singlet-triplet separation, especially for the molecules with small numbers of double bonds.

An explanation for the absorption-fluorescence gap might be sought along the following lines. The transition in ethylene which is now called $N \rightarrow V$ has according to theory a curious effect.[10] Namely, while the N state is most stable when the molecule is plane, the V state should have a very deep energy minimum when the two CH_2 groups are oriented with their planes perpendicular. When light is absorbed in the $N \rightarrow V$ region, the strongest absorption, according to the Franck-Condon principle, leaves the molecule with the two CH_2 groups still nearly in the same plane in the first instant after absorption; but they should then begin a relative rotation, which should carry them back and forth through the perpendicular orientation. This state of affairs affords an explanation of *cis-trans* photo-isomerization in ethylene derivatives.[11]

It is somewhat appalling to think what would happen in the polyenes if the $N \rightarrow V$ absorption transitions, in particular $N \rightarrow V_1$, set all the C=C

[9] See especially Hausser's Fig. 17 (reference 2) and Hausser, Kuhn, and Kuhn's Fig. 18 (p. 446 of reference 3).

[10] R. S. Mulliken, Phys. Rev. **41**, 754 (1932), especially Fig. 1; and later papers. In this figure, the levels marked $^1\Gamma_{4u}$ and $^3\Gamma_{4u}$ for plane C_2H_4 are our V and T levels.

[11] Reference 10; cf. also A. R. Olson, Trans. Faraday Soc. **27**, 69 (1931).

bonds to twisting in the same way that $N \rightarrow V$ makes the one C=C bond twist in C_2H_4. A little consideration shows, however, that such wholesale twisting is not to be expected, unless for some of the higher frequency $N \rightarrow V$ transitions or in the lowest polyenes. Since only one bonding unsaturation electron out of several is excited, and that one from the least strongly bonding of the unsaturation-electron MO's if we are dealing with $N \rightarrow V_1$, it seems probable that the plane form of the molecule remains the stable form in state V_1 for all polyenes with the possible exception of dienes. Hence the foregoing does not help us to explain the absorption-fluorescence gap, which is especially large with the longer polyene chains.

A reasonable explanation may, however, be given as follows. Applying the Franck-Condon principle to the interpretation of the observed spectrum, it is clear that the state V_1 differs somewhat from N as regards the equilibrium shape of the molecule, since the spectrum shows two series of bands excited with considerable intensity. These two series of bands correspond to excitation of two modes of vibration of rather high frequency which can be identified as polyene chain vibrations of the respective final state after absorption or fluorescence.[2, 3] But the first band, which is fairly strong and (aside from the inevitable zero point vibration) would be expected to correspond to a pure electronic transition and thus to be identical in absorption and fluorescence, actually has its peak at a higher frequency in absorption than in fluorescence. This is what we have to explain.

Now let us suppose that the equilibrium configurations of the N and V_1 states of the molecule differ not only in respect to shrinkings or stretchings of the bonds along the polyene chain, but also by a rather large deformation of the whole molecule, such as would be obtained by relative bendings between remote parts of it, without affecting, however, the planeness of the arrangement. While the bond stretchings or shrinkings should be associated with the observed excitation of fairly high frequency vibrations, the deformation may correspond to vibrations of very low frequency, and perhaps to a considerable variety of these. The deformation *energy* corresponding to the difference in equilibrium configuration between the N and V_1 states may, however, be relatively small.

According to the Franck-Condon principle, absorption (or emission) processes starting from vibrationless molecules in either electronic state would occur only with very small probability going to the equilibrium configuration of the other state. Transitions with a maximum of probability, on the other hand, would lead to a condition in which the above-mentioned low frequency vibrations would be considerably excited. Each of the observed apparently homogeneous strong bands with sharp peaks would then really represent a close superposition of a large number of deformation-frequency sub-bands spreading on both sides of the observed peak. The position of the first strong peak would then represent zero quantum numbers with respect to the high frequency vibrations but not with respect to the low frequency deformation vibrations. Because of the deformation-energy left in the molecule at the first peak, the latter would have a somewhat higher frequency in absorption and a somewhat lower frequency in fluorescence than that of the pure electronic transition. The observed facts would thus be explained.

The true position of the pure electronic transition would then be located somewhere between the first absorption peak and the first fluorescence peak, approximately at the bottom of the valley[9] separating the two. The fact that the observed width of this valley or gap increases with increase in length of the polyene chain appears to be entirely reasonable on the basis of the present explanation.

In the foregoing discussion we have assumed absorption or emission starting with vibrationless molecules. In the case of fluorescence there is good reason to believe that this condition is fulfilled for most of the emitting molecules. The observed fluorescence spectrum,—as is generally true for polyatomic and even for many diatomic molecules,—is entirely independent of the absorbed frequency by which it is excited. This indicates that practically all vibrational energy in state V_1 is lost, by collisions or otherwise, after absorption and before fluorescence. Some of the low frequency vibrational energy might, however, be retained by *some* of the molecules,

corresponding to a state of thermal equilibrium as regards the vibrations.

In the case of absorption at room temperature, an appreciable fraction of molecules would doubtless be initially in excited states as regards low frequency vibrations. This would have the effect of producing a long wave-length tail on each of the observed absorption bands, but should presumably not much affect the observed positions of their maxima. Transitions deviating in various degrees from the Franck-Condon principle would also contribute to such long wave-length tails. At very low temperatures, the part of the tail due to initially-vibrating molecules would disappear, while at high temperatures it would be intensified and the maximum might perhaps be somewhat shifted in addition.

Without attempting a detailed examination of existing data, the reader can see that our expectations are reasonably fulfilled in a figure given by Hausser and Kuhn showing the absorption and fluorescence spectra of diphenyl-octatetraene dissolved in xylol at 20°C and at −196°C. At 20°C the intensity falls to a very low minimum in both absorption and fluorescence at the middle of the absorption-fluorescence gap; the first band in each case tails off toward this gap as expected. At −196°C the tailing off is much more rapid so that there is a real empty space in the middle. The change may be attributed to removal of the thermal vibrational tailing-off, leaving only the Franck-Condon vibrational tailing-off, which is apparently relatively rapid. There is also a temperature shift in the peak of the first band, especially in the absorption spectrum; the absorption and fluorescence peaks are closer together at lower temperatures. In a complete explanation, the effects of rotational structure and of the solvent should be considered. So far as can be seen without doing this, the data seem to be consistent with the explanation given above.

Supplementary Notes for Papers III–VII, *added in proof.* —A photograph just received from Dr. W. C. Price of Cambridge University shows the absorption spectrum of butadiene vapor from λ2200 to λ1100. This is in general agreement with Scheibe and Grieneisen's figure, except that there is a broad maximum of intensity at about 58,000 cm^{-1} instead of a minimum at 57,000 cm^{-1}. [In addition, there are several sharp narrow bands between here and 50,000 cm^{-1}, in agreement with S. and G.] This maximum, which may be identified with the transitions $N \rightarrow V_2$ and $N \rightarrow V_3$ according to III, looks about a fifth as intense as $N \rightarrow V_1$. If the identification and the estimate are correct, this indicates (see III) the presence of about 20 percent of *cis* molecules in the vapor, with the remainder *trans*, instead of all being *trans* as was tentatively concluded in III and VI.

If there is really a mixture of *cis* and *trans* molecules in butadiene and its open-chain derivatives at room temperature, the relative intensities of the $N \rightarrow V_1$ and $N \rightarrow V_2$, V_3 regions should show marked variation with temperature (also perhaps between liquid and vapor). This effect and a correlated variation of molecular refractivity with temperature should then give a means of studying the energy and equilibrium relations between *cis* and *trans* isomers.

Dr. Price also sent interesting new vacuum spectrograms of thiophene, benzene, ethylene and other molecules. Thiophene, like benzene, shows a very strong absorption region with a maximum between λ1750 and λ1800. This can probably be explained along the lines discussed in IV; the resemblance to benzene may be somewhat accidental. Price confirms the occurrence (discussed in IV) of much weaker absorption in thiophene between λ2200 and λ2380; in Price's picture this appears in the form of groups of rather narrow bands. There seems to be no other absorption between the two regions just mentioned.

In II (pp. 30–31) and V the benzene absorption extending from about λ2050 to λ1600 was all attributed to $N \rightarrow V$. However, the fact that this is divided (definitely, according to Price's new photographs) into a weaker region (maximum near λ1970) and a much stronger region which fits as a Rydberg series member (maximum near λ1780) has not been explained very satisfactorily. Ethylene, according to Price, presents a similar difficulty in still more pronounced fashion. Very likely there is in these and similar cases a juxtaposition or often a partial quantum-mechanical mixing of V and other upper levels in this border region of the spectrum between sub-Rydberg and definitely Rydberg transitions (cf. II, p. 21). This subject is in need of, and offers an interesting field for, future clarification. Fortunately in the higher polyenes and their derivatives, $N \rightarrow V_1$ is at such long wave-lengths that there is no possibility of its being mixed with or confused with Rydberg transitions; and for these molecules the $N \rightarrow V$ theory is clearly in harmony with the observational data.

In connection with the discussion of hyperconjugation in IV and VI, it should have been pointed out that observed wave-length shifts and exaltations of refractivity resulting from alkyl substitution might be explained or partly explained by variations in charge accumulation (discussed in earlier papers of Price and the writer[12]) rather than by hyperconjugation. However, the pronounced long wave-length shifts of $N \rightarrow V_1$ in cyclopentadiene, thiophene and cyclohexadiene as compared with the corresponding open-chain dienes could hardly be explained in a reasonable way by such charge effects.

[12] R. S. Mulliken, J. Chem. Phys. 3, 514 (1935).

Antisymmetric Molecular Orbitals

II. Calculation of Integrals*

A. L. SKLAR
Department of Physics, The Catholic University of America, Washington, D. C.

AND

R. H. LYDDANE
Department of Physics, University of North Carolina, Chapel Hill, North Carolina

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The integrals which are common to the application of the method of antisymmetric molecular orbitals to unsaturated as well as to aromatic molecules are tabulated. Accordingly, all integrals are evaluated with $2p\pi$ hydrogen-like functions. Tables are given for the Coulomb $(aa;bb)$, exchange $(ab;ab)$, and hybrid Coulomb exchange $(ab;bb)$ repulsions of two electrons, and for the Coulomb and exchange attraction of a carbon ion for an electron.

IN A previous paper[1] the method of antisymmetric molecular orbitals was extended and applied to a calculation of the lower excited levels of the benzene molecule. The advantages of this method are the inclusion of repulsions between electrons, the diminution of polar terms through the Pauli principle, and the explicit evaluation of all interactions.

The failure to include electronic repulsions has been perhaps the most serious limitation of calculations with more simplified orbitals. It has been pointed out, for example, by F. London, and Van Vleck[2] that the simplified orbitals are useless for calculations of activation energies since they yield potential valleys instead of mountains near the united molecule. That is, for instance, H_3 turns out to be more stable than H_2+H. This contradiction is presumably traceable to the neglect of electronic repulsion whose effect opposes the stabilization introduced by the greater freedom which the electrons have in the presence of the added nucleus. It accordingly seems that the present method may extend the range of applicability of the orbitals.

Furthermore the antisymmetrization of the wave function forbids more than two electrons to accumulate, in a given state, on one nucleus. This cooperates with the repulsion of the electrons in diminishing the appearance of polar terms in which many or even all the electrons accumulate on one nucleus. The direct calculation of the interaction integrals avoids the uncertainties involved in the use of resonance energies.

The method of antisymmetric molecular orbitals applied to polyatomic molecules yields final expressions in terms of a large number of integrals. The many integrals dependent upon the geometry of the particular molecule will be treated in a forthcoming paper. Here only those common to unsaturated as well as aromatic molecules will be considered. The integrals arise from two types of interaction: the repulsion of two π electrons and the attraction of a π electron by a carbon ion.

Since the characteristic properties of aromatic and of unsaturated molecules, e.g., *cis-trans* isomerism or directing power, are due to the $2p\pi$ electrons,[3] we must use $2p\pi$ wave functions in all integrals instead of the $1s$ and $2s$ functions used in previous treatments.

COULOMB AND EXCHANGE INTEGRALS

We will define

$$(ab;cd)=\int a(1)c(2)(2/r_{12})b(1)d(2)d\tau_1 d\tau_2, \quad (1)$$

* This research was supported by a grant from the Penrose Fund of the American Philosophical Society.

[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938). (This is the first paper of this sequence.)

[2] J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 217 (1935).

[3] E. Hückel, Zeits. f. Physik **70**, 204 (1931); **72**, 310, (1931); **73**, 628 (1932); Zeits. f. Elektrochem. **43**, 827 (1937). J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).

where $a(1)$ is the real $2p\pi$ function for the first electron:[4]

$$a(1)=(Z^5/32\pi)^{\frac{1}{2}}a_1e^{-Za_1/2}\sin\theta_{a1}\cos\varphi_{a1}. \quad (2)$$

Now the Coulomb integral $(aa;bb)$ and the exchange integral $(ab;ab)$ have already been evaluated[5] with the complex $2p\pi$ functions:

$$\alpha(1)=(Z^5/64\pi)^{\frac{1}{2}}a_1e^{-Za_1/2}\sin\theta_{a1}e^{\pm i\varphi_{a1}}. \quad (3)$$

The integrals with real functions can, however, be obtained from integrals with complex functions through the following transformation formulae:

$$\begin{aligned}(aa;bb)&=(\alpha\alpha;\beta\beta)+\tfrac{1}{2}\int[\alpha(1)\beta(2)]^2\\&\quad\times(2/r_{12})\cos 2(\varphi_1-\varphi_2)d\tau_1d\tau_2,\\(ab;ab)&=(\alpha\beta;\alpha\beta)+\tfrac{1}{2}\int\alpha(1)\beta(1)\alpha(2)\beta(2)\\&\quad\times(2/r_{12})\cos 2(\varphi_1-\varphi_2)d\tau_1d\tau_2.\end{aligned} \quad (4)$$

For small values of ρ, where $\rho=ZR$, Bartlett has given all four of the integrals necessary for $(aa;bb)$ and $(ab;ab)$ which latter appear in Table I. The values of the integrals for large values of ρ were obtained by developing approximation formulae which are valid for large ρ and by extrapolating Bartlett's tables for small quantities.

TABLE I.[6]

ρ	6	8.37	10	12	14.5	16.7	20
$(aa;bb)/Z$	0.262	0.209	0.181	0.155	0.131	0.115	0.097
$(ab;ab)/Z$	0.073	0.022	0.0082	0.0031	0.0006	0.0001	0.0000

It is also necessary to consider the mutual potential energy of the two $2p\pi$ electrons situated on the same carbon atom. Expanding $1/r_{12}$ in spherical harmonics,[7] the integral $(aa;aa)$ may be expressed in closed form:

$$(aa;aa)=0.3881Z.$$

THE HYBRID COULOMB-EXCHANGE INTEGRAL $(ab;bb)$

In calculations with polyatomic molecules there occur many interactions besides the Coulomb and exchange ones. The most important of these additional interactions is the hybrid Coulomb-exchange integral $(ab;ab)$, since it is intermediate between the Coulomb and exchange values. Now $(ab;bb)$ has only been evaluated with $2s$ functions for molecules like H_2 and Be_2.[8] In the case of double bonds we must use $2p\pi$ functions instead.

The integral has then the form

$$\int a(1)b(1)b^2(2)(2/r_{12})d\tau_1d\tau_2. \quad (5)$$

If one introduces polar coordinates $(a_i,\ \theta_{ai},\ \varphi_i)$ and $(b_i,\ \theta_{bi},\ \varphi_i)$ whose origins are, respectively, at the first nucleus and at the second nucleus, and whose polar axes are along the line joining the two nuclei, the integral reads:

$$(ab;bb)=(Z/32\pi)^2\int e^{-(Z/2)(a_1+b_1)}a_1b_1\sin\theta_{a1}\sin\theta_{b1}\cos^2\varphi_1d\tau_1\int e^{-Zb_2}b_2\sin^2\theta_{b2}\cos^2\varphi_2(2/r_{12})d\tau_2. \quad (6)$$

One can immediately expand $(2/r_{12})$ in the well-known series involving spherical harmonics[9] and carry out the integration over the coordinates of the second electron[7] and over φ_1:

$$(ab;bb)=\frac{8\pi^2c^4}{15Z^4R}\int e^{-(Z/2)(a_1+b_1)}a_1b_1\sin\theta_{a1}\sin\theta_{b1}\{5g_{5,\,1}(Zb_1)-[P_2(\cos\theta_{b1})-\tfrac{1}{4}P_2^2(\cos\theta_{b1})]\times g_{7,\,3}(Zb_1)\}a_1da_1b_1db_1. \quad (7)$$

[4] a_1, θ_{a1}, φ_{a1} are the polar coordinates of electron 1 with respect to a coordinate system at nucleus a.
[5] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).
[6] All quantities in this paper are in atomic units. R is the internuclear distance.
[7] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).
[8] J. H. Bartlett, Jr. and W. H. Furry, Phys. Rev. **38**, 1615(1931).
[9] E. W. Hobson, *Spherical and Ellipsoidal Harmonics* (Cambridge, 1931), p. 145.

Introducing new variables $\alpha=Za_1$, $\beta=Zb_1$, $\rho=ZR$ and replacing sines and cosines by their values in terms of α, β and ρ, one has

$$\frac{(ab;bb)}{Z}=\frac{1}{7680\rho^3}\int e^{-(\alpha+\beta)/2}[4\beta^2\rho^2-(\beta^2+\rho^2-\alpha^2)^2] \times\left\{5g_{5,1}(\beta)-\left[\frac{9(\beta^2+\rho^2-\alpha^2)^2}{16\beta^2\rho^2}-\frac{5}{4}\right]g_{7,3}(\beta)\right\}\alpha d\alpha\beta d\beta, \quad (8)$$

where $g_{5,1}(\beta)=(1/\beta)[24-e^{-\beta}(\beta^3+6\beta^2+18\beta+24)]$,

$g_{7,3}(\beta)=(5/\beta)[144-e^{-\beta}(\beta^5+6\beta^4+24\beta^3+72\beta^2+144\beta+144)]$.

If one defines the quantities (for $s, t\geqslant 0$)

$$I(s,t)=\tfrac{1}{2}e^{\rho/2}\int e^{-(\alpha+\beta)/2}\alpha^s\beta^t d\alpha d\beta,$$

$$J(s,t)=\tfrac{3}{2}e^{\rho/2}\int e^{-\alpha/2}e^{-3\beta/2}\alpha^s\beta^t d\alpha d\beta,$$

$$K(s)=\tfrac{1}{2}e^{\rho/2}\int e^{-(\alpha+\beta)/2}(1-e^{-\beta})\alpha^s\beta^{-1}d\alpha d\beta,$$

$$A_s=e^{2\rho}\int_\rho^\infty e^{-2\alpha}\alpha^s d\alpha,$$

$$C_s=e^{\rho}\int_\rho^\infty e^{-\alpha}\alpha^s d\alpha,$$

$$D_s=e^{\rho}s!-C_s,$$

one can after a considerable amount of rearrangement and integration by parts write the integral

$$(ab;bb)/Z=(1/256\rho^5)e^{-\rho/2}\{\Sigma_1-\Sigma_2+\tfrac{1}{2}\Sigma_3-(27/2)(\Sigma_4+\Sigma_5+e^{-\rho}\Sigma_6)\}, \quad (9)$$

where $\Sigma_1=(162-8\rho^2)I(5,0)+(-108+16\rho^2)I(3,2)+(12\rho^2+16\rho^4)I(3,0)+(27-8\rho^2)I(1,4)$
$+(-60\rho^2+16\rho^4)I(1,2)+(66\rho^4-8\rho^6)I(1,0)$.

$\Sigma_2=(1/16)J(9,1)+(3/8)J(9,0)-(1/4)J(7,3)-(3/2)J(7,2)-(6+(1/4)\rho^2)J(7,1)-(18$
$+(3/2)\rho^2)J(7,0)+(3/8)J(5,5)+(9/4)J(5,4)+(9+(1/4)\rho^2)J(5,3)+(27+(3/2)\rho^2)$
$\times J(5,2)+(54+(20/3)\rho^2+(3/8)\rho^4)J(5,1)+(54+(70/3)\rho^2+(9/4)\rho^4)J(5,0)-(1/4)$
$\times J(3,7)-(3/2)J(3,6)+(-6+(1/4)\rho^2)J(3,5)+(-18+(3/2)\rho^2)J(3,4)+(-36$
$+(14/3)\rho^2+(1/4)\rho^4)J(3,3)+(-36+(22/3)\rho^2+(3/2)\rho^4)J(3,2)+(4\rho^2+(14/3)\rho^4$
$-(1/4)\rho^6)J(3,1)+(4\rho^2+(22/3)\rho^4-(3/2)\rho^6)J(3,0)+(1/16)J(1,9)+(3/8)J(1,8)$
$+((3/2)-(1/4)\rho^2)J(1,7)+((9/2)-(3/2)\rho^2)J(1,6)+(9-(16/3)\rho^2+(3/8)\rho^4)J(1,5)$
$+(9-(38/3)\rho^2+(9/4)\rho^4)J(1,4)+(-20\rho^2+(23/3)\rho^4-(1/4)\rho^6)J(1,3)+(-20\rho^2$
$+(49/3)\rho^4-(3/2)\rho^6)J(1,2)+(22\rho^4-(16/3)\rho^6+\rho^8)J(1,1)+(22\rho^4-\rho^6+\rho^8)J(1,0)$.

$\Sigma_3=(9/16)K(9)-(54+(9/4)\rho^2)K(7)+(78\rho^2+(27/8)\rho^4)K(5)+(6\rho^4-(9/4)\rho^6)K(3)$
$+(-30\rho^6+(9/16)\rho^8)K(1)$.

$\Sigma_4=(1/60480)(-443\rho^9+1818\rho^8+66208\rho^7)+(181/12)\rho^5-(107/9)\rho^4-(4195/8)\rho^3-(14279/6)\rho^2$
$-(637065/128)\rho-(277815/64)$.

$\Sigma_5=(1/24)C(8)-((1/12)+(3/8)\rho)C_7+(-(11/3)+(3/4)\rho+(4/3)\rho^2)C_6+(25\rho-(8/3)\rho^2$
$-(7/3)\rho^3)C_5+(-(608/9)\rho^2+(14/3)\rho^3+2\rho^4)C_4+((832/9)\rho^3-4\rho^4-(2/3)\rho^5)C_3$
$+(-(592/9)\rho^4+(4/3)\rho^5)C_2+(176/9)\rho^5C_1$.

$\Sigma_6=-(1/8)(A_8+D_8)+(-(1/4)+(9/8)\rho)(A_7+D_7)+((11/3)+(9/4)\rho-4\rho^2)(A_6+D_6)$
$+(-25\rho-8\rho^2+7\rho^3)(A_5+D_5)+((608/9)\rho^2+(14/3)\rho^3-6\rho^4)(A_4+D_4)+(-(832/9)\rho^3$
$-12\rho^4+2\rho^5)(A_3+D_3)+((592/9)\rho^4+4\rho^5)(A_2+D_2)-(176/9)\rho^5(A_1+D_1)$.

The evaluation is thus reduced to the computation of the quantities $I(s, t)$, $J(s, t)$, $K(s)$, A_s, C_s, and D_s, which can be accomplished by the recursion formulae now to be developed.

Consider for example $I(s,t)$:

$$I(s,t)-2tI(s,t-1)=(1/2)e^{\rho/2}\int_0^\infty e^{-\alpha/2}\alpha^s d\alpha\int_{|\alpha-\rho|}^{\alpha+\rho} e^{-\beta/2}(\beta^t-2t\beta^{t-1})d\beta$$

$$=-\int_0^\infty e^{-\alpha}\alpha^s(\alpha+\rho)^t d\alpha+e^\rho\int_\rho^\infty e^{-\alpha}\alpha^s(\alpha-\rho)^t d\alpha+\int_0^\rho \alpha^s(\rho-\alpha)^t d\alpha.$$

Writing $i(s, t)$ for the sum of the first two terms above and $j(s, t)$ for the third, one has:

$$I(s,t)-2tI(s,t-1)=i(s,t)+j(s,t). \quad (10)$$

$i(s, t)$ and $j(s, t)$ can now be found easily by the same sort of treatment; one finds:

$$\left.\begin{aligned} &i(s,t)=si(s-1,t)+ti(s,t-1)\\ &i(s,0)=-i(0,s)=C_s-s!\\ &(s+1)j(s,t)=tj(s+1,t-1)\\ &j(s,0)=\rho^{s+1}/s+1. \end{aligned}\right\} \quad (11)$$

Furthermore, $I(s, 0)=i(s, 0)+j(s, 0)$.

The same method of procedure applied to $J(s, t)$ gives

$$J(s,t)-(2t/3)J(s,t-1)=f(s,t)+g(s,t) \quad (12)$$
$$J(s,0)=f(s,0)+g(s,0).$$

$$\left.\begin{aligned} &f(s,t)=-sf(s-1,t)+tf(s,t-1)\\ &f(s,0)=B_s\\ &f(0,t)=-\rho^t e^{-\rho}+tf(0,t-1)\\ &g(s,t)=(s/2)g(s-1,t)+(t/2)g(s,t-1)\\ &g(s,0)=A_s-e^{-\rho}(s!/2^{s+1})\\ &g(0,t)=e^{-\rho}\rho^t/2+(t/2)g(0,t-1), \end{aligned}\right\} \quad (13)$$

where $$B_s=e^{-\rho}\int_0^\rho e^\alpha\alpha^s d\alpha.$$

For $K(s)$ one obtains:

$$K(s)-2sK(s-1)=m(s)+n(s). \quad (14)$$

$$\left.\begin{aligned} &K(0)=\gamma+\ln(\rho/2)-(1+e^{-\rho})Ei(-\rho)\\ &\qquad\qquad +e^\rho Ei(-2\rho)\\ &m(s)=(s-1)![1-(e^{-\rho}/2^s)]-\rho m(s-1)\\ &m(1)=1-(e^{-\rho}/2)+\rho e^\rho[Ei(-\rho)\\ &\qquad\qquad -Ei(-2\rho)]\\ &n(s)=A_{s-1}+B_{s-1}-C_{s-1}+\rho n(s-1)-\rho^s/s\\ &n(1)=A_0+B_0-C_0+\rho[\gamma+\ln(\rho/2)\\ &\qquad\qquad -1-Ei(-\rho)]. \end{aligned}\right\} \quad (15)$$

Finally it is necessary to compute A_s, B_s and C_s. (D_s follows directly from C_s.)

$$\left.\begin{aligned} &A_s=\rho^s/2+\tfrac{1}{2}sA_s-1 && A_0=\tfrac{1}{2}\\ &B_s=\rho^s-sB_{s-1} && B_0=1-e^{-\rho}\\ &C=\rho^s+sC_{s-1} && C_0=1. \end{aligned}\right\} \quad (16)$$

TABLE II. $I(s, t)$.

s \ t	0	1	2
	$\rho=6$		
0	6		
1	24		
2	120	396	
3	684	2260.8	10828.8
4	4291.2	14889.6	
5	29232		
	$\rho=8.37$		
0	8.37		
1	43.399		
2	282.26	1060.31	
3	2073.8	7308.7	37180
4	16511.0	57207	
5	139861		
	$\rho=10$		
0	10		
1	60		
2	453.33	1860	
3	3860	14440	77867
4	35440	126533	
5	343870		
	$\rho=14.5$		
0	14.5		
1	119.625		
2	1255.46	6433.9	
3	14817.6	66168	428540
4	187465	761940	
5	24864000		

These last quantities are obtained with such ease that we do not give tables of their values. The evaluation of $I(s,t)$, $J(s,t)$ and $K(s)$, however, is long and complicated, and since these quantities appear also in other problems we have tabulated them in Tables II, III and IV, respectively. The integral $(ab;bb)$ appears in Table V. The column $\rho=8.37$ was calculated instead of 8 because it corresponds to the $C=C$ distance in aromatic compounds and to the present best choice of effective charge for the C atom;[10] the 14.5 and 16.7 columns are, respectively, $8.37\times(3)^{\frac{1}{2}}$ and 2×8.37.

TABLE III.

$J(s,t)$

$\rho=6$

t \ s	1	3	5	7	9
0	8.2519	277.89	10263.7	410500	17848400
1	11.2667	357.90	13567.9	592190	29576000
2	23.030	684.56	26864	1292920	
3	62.239	1730.78	70843	3771100	
4	207.19	5430.9	233290		
5	811.50	20334	920740		
6	3622.9	88418			
7	18026.3	437730			
8	98367				
9	581880				

$\rho=8.37$

0	11.8052	772.81	53385	3858200	291.30×10^6
1	16.5845	1017.22	69475	5169700	416.32×10^6
2	35.340	1996.99	134752	10400400	
3	101.015	5194.3	346610	27910000	
4	360.97	16775.3	1109630		
5	1538.75	64569	4249000		
6	7565.3	288040			
7	41822	1459440			
8	254950				
9	1688570				

$\rho=10$

0	14.2500	1336.88	130494	13170200	1371.67×10^6
1	20.251	1784.25	170376	17359500	1876.17×10^6
2	43.881	3565.9	331560	34220000	
3	128.328	9474.5	855250	89734000	
4	472.44	31338	2743200		
5	2090.5	123749	10510300		
6	10749.2	566780			
7	62595	2948000			
8	404490				
9	2854200				

$\rho=14.5$

0	21.000	4192.1	854140	177.124×10^6	37330×10^6
1	30.375	5755.8	1137430	232.85×10^6	49203×10^6
2	67.500	11944.3	2269300	457.11×10^6	
3	204.19	33246	6026000	1191.40×10^6	
4	785.29	116146	19957700		
5	3671.0	487980	79100000		
6	20195	2392500			
7	127540	13384400			
8	906590				
9	7136200				

[10] C. Zener, Phys. Rev. **36**, 51 (1930).

TABLE IV. $K(s)$.

s \ ρ	6	8.37	10	14.5
1	8.3255	13.2740	17.0074	28.398
3	254.02	737.94	1322.12	4543.4
5	10035.3	50157	123111	845380
7	490880	3896200	12773300	169.91×10^6
9	30748000	345.71×10^6	1460.18×10^6	36146×10^6

TABLE V.

ρ	6	8.37	10	12	14.5	16.7	20
$(ab;bb)/Z$	0.3245	0.10341	0.05342	0.0240	0.0092	0.0038	0.001

PENETRATION INTEGRALS

The attraction of the ring skeleton upon the π electrons must now be considered (the ϵ_l of the previous paper[1]). The ring skeleton consists of carbon atoms each lacking one π electron. Instead of calculating directly the attraction of an ion we may add and subtract a π electron. This gives the potential of the carbon ion, H_K, as the potential of a neutral carbon atom, $\mathbf{H}$, minus the potential of a π electron.

$$H_K(\nu)=\mathbf{H}_K(\nu)-\int\frac{e^2}{r_{\nu\mu}}K^2(\mu)d\tau_\mu.$$

The effect of the second term on a π electron has already been evaluated as an $(aa;bb)$ integral. This leaves us only the effect of the spherically symmetrical neutral carbon atom. It was shown in the preceding paper that the attraction of a neutral carbon atom may be written:

$$\mathbf{H}=-\int_{r_\nu}^{\infty}\left(\frac{r}{r_\nu}-1\right)\sigma(r)rdr,$$

where

$$\sigma(r)=4\pi\{|\psi_{2s}|^2+|\psi_{2px}|^2+|\psi_{2py}|^2+|\psi_{2pz}|^2\}.$$

We will let

$$Q_{kl}=-\int\mathbf{H}_I(\nu)K(\nu)L(\nu)d\tau_\nu. \qquad (17)$$

The Coulomb penetration integral Q_{ll} can be obtained by direct integration. The Coulomb penetration of a π electron on nucleus 2 within

the spherical distribution, **H**, about nucleus 1 is found to be:

$$Q_{22}(\rho)=\frac{Z}{3840}e^{-\rho}\left\{\frac{4}{7}\rho^5+\frac{67}{7}\rho^4+46\rho^3+461\rho^2+1125(\rho+1)\right\}. \quad (18)$$

The exchange penetration integral Q_{12} can be obtained in terms of the $J(s, t)$:

$$\begin{aligned}Q_{12}=(Z/512\rho^3)\{&-J(5,3)-4J(5,2)\\&-12J(5,1)-16J(5,0)+2J(3,5)\\&+8J(3,4)+24J(3,3)+32J(3,2)\\&-J(1,7)-4J(1,6)-12J(1,5)\\&-16J(1,4)+\rho^2(2J(3,3)+8J(3,2)\\&+24J(3,1)+32J(3,0)+2J(1,5)\\&+8J(1,4)+24J(1,3)+32J(1,2))\\&-\rho^4(J(1,3)+4J(1,2)+12J(1,1)\\&+16J(1,0))\}\tfrac{2}{3}e^{-\frac{1}{2}\rho}.\end{aligned} \quad (19)$$

TABLE VI.

ρ	6	8.37	10	12	14.5	16.7	20
Q_{22}/Z	0.0773	0.01976	0.00703	0.00182	0.000312	0.000058	0.0_646
Q_{12}/Z	0.1200	0.04364	0.02090	—	—	—	—

Accordingly, this integral may be immediately obtained from Table III.

The values of Q_{22} and Q_{12} are given in Table VI.

If one neglects all interactions, except Coulomb, of electrons on atoms farther apart than neighbors, as is usually done, the only integrals which appear in any calculation with antisymmetric molecular orbitals are the ones treated in in this paper. The validity of this approximation will be discussed in a forthcoming publication.

The authors wish to express their thanks to Professor K. F. Herzfeld and Dr. M. Goeppert-Mayer for their interest in this calculation.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Raman Effect of Concentrated Electrolytic Solutions

Our ideas of the structure of liquid water have become clearer of recent years, thanks to the improvement in the methods of infra-red, Raman effect and x-rays, but, in the field of electrolytic solutions, particularly of the concentrated ones, the same doubts exist as to certain hypotheses more or less expressly set forth by various authors. However, it is clear that the study of these solutions by any of those methods can furnish data enabling us to make those hypotheses precise, and it may possibly even cause us to modify several recent conclusions relating to liquid water.

We have had the opportunity of returning to the study of these solutions by the Raman effect, and this letter describes several early results obtained. The solutions are ultra-filtered by means of collodion films under their own pressure.[1] The exciting light is filtered by means of inorganic filters which are practically unalterable. The voltage at the terminals of mercury lamps is kept constant within ±1.5 volts by means of an intensity regulator. The time of exposure is chosen between 1 and 5 days, so that the continual background be very low. The exciting lines are λλ4047 and 4358A.

In Table I Raman frequencies are given in cm^{-1} for solutions of $ZnCl_2$, $Zn(NO_3)_2$, $ZnSO_4$, $Zn(ClO_4)_2$, $Cu(NO_3)_2$ and H_2O at 15.5°C. Those marked with an asterisk had never yet been observed by any experimenter; those marked with a bar (—) are easily identified; the numbers between brackets show the intensity measured by comparison with graded spectrums of a standard lamp, obtained on the same plate, without analysis of microphotometric curves, and are generally found to be accurate within 5 percent. This analysis alters the relative intensities of certain bands as well as the frequency of their maxima, but this will only be shown in a later communication. An interrogation point implies that we were unable to determine the intensity under present conditions, or that the uncertainty is decidedly greater than 5 percent.

$\Delta\nu \approx 1644$ is the deformation frequency of H_2O; it is

TABLE I.

$ZnCl_2$ (9.13 *M*)	$Zn(NO_3)_2$ (4.55 *M*)	$ZnSO_4$ (3.32 *M*)	$Zn(ClO_4)_2$ (3.19 *M*)	H_2O	$Cu(NO_3)_2$ SATURATED†
* 108 (40 ?)	—	—	—	—	—
* 188 (?)	* 203 (?)	* 188 (60.0)	* 183 (27.0)	167 (57.5)	* 279 (*m*)
286 (40 ?)	—	—	—	—	—
378 (16 ?)	* 383 (5.7)	* 393 (16.0)	* 393 (18.6)	—	* 442 (*F*)
—	—	414 (34.3)	459 (59.0)	—	—
*b** 500–700 (?)	*b** 500–700 (?)	*b** 500–700 (?)	*b** 500–700 (?)	*b* 454 (12.1) *b* 788 (7.3)	?
—	—	610 (21.5)	* 625 (45.5)	—	—
—	* 717 (5.0) 670 (?)	—	—	—	* 717 (*f*) 754 (*m*)
—	* 817 (?) 901 (?)	—	—	—	*b** 830 (*f*)
—	—	973 (100.0)	* 929 (120 ?)	—	—
—	1041 (88.0)	1107 (13.0)	* 1102 (16.6)	—	1048 (*F*)
—	* 1343 (16.2) 1413 (20.8)	—	—	—	1325 (*F*) * 1421 (*F*) 1476 (*F*)
* 1646 (16 ?)	* 1646 (10.8)	* 1646 (5.8)	* 1633 (8.2)	* 1637 (8.0)	* 1654 (*m*)

b = band; *F* = strong; *m* = mean; *f* = weak.

† The results with $Cu(NO_3)_2$ have been published already—Comptes rendus **195**, 652 (1932).

generally rather intense in solutions, as already shown.[2] Zn^{++} is therefore at least as satisfactory as Mg^{++} and Ca^{++} in stimulating the intensity of this band contrary to what has often been stated in literature. This fact deserves our very careful attention. $\Delta\nu=817$–901 of $Zn(NO_3)_2$ probably corresponds to the inactive frequency in the

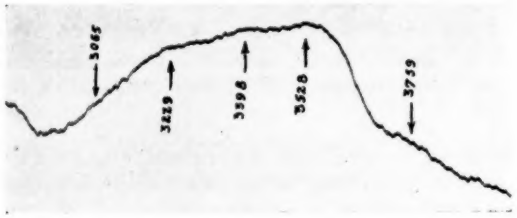

FIG. 1. Microphotogram of Raman band of water ≈ 3400 cm^{-1} in $Zn(ClO_4)_2$ solution.

Raman effect of the ion NO_3^- which is supposed to be flat. This may however have the shape of a very flattened pyramid, and the fact that, according to wave mechanics, there is a finite probability of the passing of N from a one position to its symmetrical one, across the barrier of the oxygens, may account for its comparatively large separation. The explanation of the undoubling up of the degenerate frequencies of NO_3^- is not obvious. In $Cu(NO_3)_2$, the highest degenerate frequency is triple; this may be explained *a priori* by the resonance $2\times717\approx1444$. We hope that experiments now being made will enable us to arrive at some conclusion pending consideration of various hypotheses. In $ZnSO_4$ $\Delta\nu=383$ may be considered an associate of $\Delta\nu=414$ (destruction of a double degeneracy of $SO_4^=$), but it is followed on the side of the minor frequencies by a shadow which testifies to the existence of an overlapping band. Something similar happens to the corresponding frequency of $ZnSO_4$, but this is not quite as clear; there seems to be, therefore, a neighboring frequency of 383, common to solutions of zinc salts. The correspondent in $Cu(NO_3)_2$ would be $\Delta\nu=442$. $\Delta\nu\approx188$ has been attributed to a hindered translation motion of the H_2O molecules. Meanwhile we propose only to observe their great intensity in solutions. Above the $\Delta\nu\approx1646$ some solutions present curious particularities not indicated in the Table I. For the present we will only mention, as an example, that the water band (?) on $Zn(ClO_4)_2$ has a very complicated structure (see microphotogram in Fig. 1) which is not found either in pure water or in the other solutions.

A work including accurate measurements of intensity must perforce be long, but we hope soon to be in a position to throw light on the facts already set forth, as well as on others which stand out from our table.

A. DA SILVEIRA

Physics Laboratory of the Higher Technical School,
Lisbon (N) Portugal,
March 10, 1939.

[1] A. da Silveira, Comptes rendus **194**, 1336 (1932).
[2] A. da Silveira and E. Bauer, Comptes rendus **195**, 416 (1932).

The Apparent Molal Ionic Volumes in Aqueous Solutions of Strong Electrolytes

This note records certain results obtained in the study of apparent ionic volumes obtained by computation from existing data. 197 electrolytes, described as "strong" in the *International Critical Tables*,[1] were selected. The data on density of solution at 20°C or 25°C were obtained in these Tables and also in Landolt and Börnstein, fifth edition.

The Debye-Hückel theory shows[2] that the variation of the apparent molal ionic volume of the electrolyte, φ, should vary linearly with the square root of the concentration, c, or

$$\varphi=\varphi_0+kc^{0.5} \tag{1}$$

and that values of k depend upon the atomic number, z, and valency, ν. $k=0.89(\nu_i z_i^2)^{\frac{1}{2}}$, of the ions.

The computations show that this linear relation is not satisfied by the major part of these electrolytes. In Table I are given the values of n, in Eq. (2),

$$\varphi=\varphi_0+kc^n, \tag{2}$$

using concentrations less than one mole per liter.

Of the 197 strong electrolytes, six have anomalous variations, showing one or more maxima or minima, or indicating no possibility of even an approximately linear relation. They are omitted from the table. Four of the 191 seem to have a linear relation, but with k negative. These are indicated by the numbers enclosed in parentheses

TABLE I. *Number of strong electrolytes having the indicated value of n in Eq. (2).*

Valency type	Approximate value of n											
	>2	2	1.8	1.0	0.8	0.5	0.4	0.3	0.25	0.2	<0.2	Total
1–1	2	2	0	18	9(1)	32	2	1	1	0	7	75
2–1	1	0	1	29	11	22(1)	4(1)	3	3	3	10(1)	90
3–1	0	0	0	4	1	3	0	1	0	0	3	12
2–2	1	1	0	2	2	4	0	0	1	0	1	12
3–2	0	0	0	0	0	0	0	0	0	2	0	2
4–1	0	0	0	0	0	0	0	0	0	0	0	0
Total	4	3	1	53	24	62	7	5	5	5	22	191

in the table. Included in the table are seven for each of which φ has negative values, but k positive. It is to be understood that the data in many cases follow the linear relation very closely, while in others the relation is only approximate.

The wide variation from $n=0.5$ indicates strongly that the simple electrostatic theory must omit one or more important factors. One of these appears to be the variation of density because of alteration of structure of the water with concentration. X-ray diffraction data in recent years has indicated that the liquid structure of water must change with increasing temperature. Data will be presented in a subsequent article that show a similar variation of structure and consequently of density, with concentration of the electrolyte.

G. W. STEWART

State University of Iowa,
Iowa City, Iowa,
March 4, 1939.

[1] *International Critical Tables*, Volumes 4 and 6.
[2] F. T. Gucker, Chem. Rev. **13**, 110 (1933).

Raman Effect of Difluoromethane

We have observed ten Raman lines for difluoromethane using our usual equipment for liquefied gases.[1, 2] The compound was passed from a tank through a copper-glass seal and liquefied in the Raman tube where it was held at a temperature of about −60°C during exposures. All connections were of glass including those to a safety system consisting of a manometer and two three-liter evacuated bulbs which would automatically catch the escaping gas if the cooling system failed while the apparatus was not being watched. Illumination was by means of eight concentric neon-mercury lamps. No filters were used. Results are shown in Table I.

TABLE I. *Raman lines of difluoromethane.*

$\Delta\nu$ cm^{-1}	% Mean Deviation	Exciting Lines			No. of Readings	Relative Intensities
532.4	0.08	*a*		*c*	5	5
746.1	.02			*c*	2	00
1054.4	.14	*a*		*c*	4	3(diff.)
1078.6	.13	*a*	*b*?	*c*	5	10
1261.7	.17	*a*	*b*	*c*	6	9
1293.5	.02			*c*	2	0(diff.)
1508.5	.08	*a*		*c*	4	3
2837.7	.05			*c*	3	4
2963.4	.06	*a*	*b*	*c*	8	10
3029.8	.02	*a*	*b*	*c*	5	5

a=4046; b=4077; c=4358A.

Eastman Spectroscopic Plates Type 1-J were used. The material was furnished by the E. I. duPont de Nemours Company and was laboratory fractionated, boiling range about 0.2°C. We wish to thank Dr. A. F. Benning of the Jackson Laboratory for the loan of this substance. Further consideration of these results will appear in a later publication.

GEO. GLOCKLER
G. R. LEADER

University of Minnesota,
Minneapolis, Minnesota,
March 9, 1939.

[1] Geo. Glockler and J. H. Bachmann, Phys. Rev. **54**, 970 (1938).
[2] Geo. Glockler and M. M. Renfrew, Rev. Sci. Inst. **9**, 306 (1938).

On the Application of the Franck-Condon Principle to the Absorption Spectrum of $HgCl_2$

Wehrli[1] has published a very interesting investigation of discrete absorption spectra of the mercury halides. Photographs have been given for $HgCl_2$ and are apparently both very simple and complete. In interpreting the spectrum Wehrli made use of selection rules derived by Herzberg and Teller,[2] and he pointed out that experiment and theory are in agreement.

TABLE I.

Previous Interpretation	New Interpretation
$v_s''=0, v_\delta''=1\rightarrow v_s'=2, v_\delta'=0$	$v_s''=1, v_\delta''=0\rightarrow v_s'=3, v_\delta'=0$
$v_s''=1, v_\delta''=0\rightarrow v_s'=0, v_\delta'=1$	$v_s''=2, v_\delta''=0\rightarrow v_s'=1, v_\delta'=2$
$v_s''=1, v_\delta''=1\rightarrow v_s'=0, v_\delta'=0$	$v_s''=2, v_\delta''=0\rightarrow v_s'=1, v_\delta'=0$*
$v_s''=2, v_\delta''=0\rightarrow v_s'=0, v_\delta'=1$	$v_s''=3, v_\delta''=0\rightarrow v_s'=1, v_\delta'=2$
$v_s''=2, v_\delta''=1\rightarrow v_s'=0, v_\delta'=0$	$v_s''=3, v_\delta''=0\rightarrow v_s'=1, v_\delta'=0$*
$v_s''=3, v_\delta''=0\rightarrow v_s'=0, v_\delta'=1$	$v_s''=4, v_\delta''=0\rightarrow v_s'=1, v_\delta'=2$
$v_s''=3, v_\delta''=1\rightarrow v_s'=0, v_\delta'=0$	$v_s''=4, v_\delta''=0\rightarrow v_s'=1, v_\delta'=0$*

* This interpretation has been mentioned also by Wehrli as an alternative possibility.

There are, however, a few points in which the given level diagram is not entirely satisfactory. In the first place, transitions occur in which the deformation vibration changes by one quantum number (e.g. the transition from $v_s''=2$, $v_\delta''=0$ to $v_s'=0$, $v_\delta'=1$). Such transitions are in contradiction to the selection rules. Secondly, transitions are absent which according to the Franck-Condon principle should occur with considerable intensity (e.g. $v_s''=1$, $v_\delta''=0\rightarrow v_s'=3$, $v_\delta'=0$, which should be stronger than $v_s''=3$, $v_\delta''=0\rightarrow v_s'=0$, $v_\delta'=0$, whereas only the second transition is given in Wehrli's diagram). Both difficulties can be removed if some small changes are made in the original interpretation. They are listed in Table I. The two interpretations predict slightly different positions for the bands in question. The new interpretation seems to fit the observation somewhat better than the old one. Thus, the band which Wehrli had called $v_s''=2$, $v_\delta''=1\rightarrow v_s'=0$, $v_\delta'=0$ does not lie in the middle between the bands $v_s''=2$, $v_\delta''=0\rightarrow v_s'=0$, $v_\delta'=0$ and $v_s''=2$, $v_\delta''=2\rightarrow v_s'=0$, $v_\delta'=0$ as would follow from his previous assumption but is a little closer to $v_s''=2$, $v_\delta''=0\rightarrow v_s'=0$, $v_\delta'=0$ as should be expected from the new interpretation. The rest of Wehrli's analysis will remain unchanged.

The spectrum of $HgCl_2$ is, according to the modified interpretation, in complete agreement with the selection rules for an allowed electronic transition. Thus, Wehrli's study of this absorption spectrum leads to results which are highly significant for the interpretation of spectra of polyatomic molecules.

The authors take pleasure in thanking Professor Wehrli for stimulating correspondence.

H. SPONER
E. TELLER

Departments of Physics,
Duke University,
Durham, N. C., and
The George Washington University,
Washington, D. C.,
April 15, 1939.

[1] M. Wehrli, Naturwiss. **25**, 734 (1937); Helv. Phys. Acta **11**, 339 (1938).
[2] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).